

UNIVERSITY OF HAWAII
LIBRARY

DEC 11 '54

ADVANCES IN PHYSICS

A QUARTERLY SUPPLEMENT
of the
PHILOSOPHICAL MAGAZINE

EDITOR

PROFESSOR N. F. MOTT, M.A., D.Sc., F.R.S.

EDITORIAL BOARD

SIR GEORGE THOMSON, M.A., D.Sc., F.R.S.

PROFESSOR A. M. TYNDALL, C.B.E., D.Sc., F.R.S.

SIR LAWRENCE BRAGG, O.B.E., M.C., M.A., D.Sc., F.R.S.

VOLUME 3

OCTOBER 1954

NUMBER 12

PRICE per part 15s. 0d.

PRICE per annum £2 15s. 0d. post free

PRINTED AND PUBLISHED BY TAYLOR & FRANCIS LTD.

RED LION COURT, FLEET ST., LONDON E.C.4

QC1
A36

Early Scientific Publications



DIARY OF ROBERT HOOKE, M.A., M.D., F.R.S.
1672-1680

Edited by **H. W. ROBINSON** and **W. ADAMS**
Recommended for publication by the Royal Society,
London

25/-
net

"This vivid record of the scientific, artistic and social activities of a remarkable man during remarkable years has too long remained in obscurity."—Extract from foreword by Sir Frederick Gowland Hopkins, O.M., President of the Royal Society.

MATHEMATICAL WORK OF JOHN WALLIS, D.D., F.R.S.

By **J. F. SCOTT, Ph.D., B.A.**

12/6
net

"His work will be indispensable to those interested in the early history of The Royal Society. I commend to all students of the Seventeenth Century, whether scientific or humane, this learned and lucid book."—Extract from foreword by Prof. E. N. da C. Andrade, D.Sc., Ph.D., F.R.S.
Recommended for publication by University of London

CORRESPONDENCE AND PAPERS OF EDMOND HALLEY

21/-
net

Arranged and Edited by **EUGENE FAIRFIELD MACPIKE**
First published on behalf of The History of Science Society by Oxford University Press. Now re-issued by Taylor & Francis, Ltd.

MEMOIRS OF SIR ISAAC NEWTON'S LIFE

5/-
net

By **WILLIAM STUKELEY, M.D., F.R.S., 175**
From an Original Manuscript
Now in the possession of the Royal Society, London

HEVELIUS, FLAMSTEED AND HALLEY

12/6
net

Three Contemporary Astronomers and their Mutual Relations
By **EUGENE FAIRFIELD MACPIKE**
Published by arrangement with The History of Science Society

Established
over 150 years

TAYLOR & FRANCIS, LTD.
RED LION COURT, FLEET ST., LONDON E.C.
PRINTERS & PUBLISHERS OF SCIENTIFIC BOOKS

CONTENTS

| | |
|---|-----|
| Twinned Crystals. By R. W. CAHN, Department of Metallurgy, University of Birmingham (temporarily at the Johns Hopkins University, Baltimore, Md., U.S.A.) | 363 |
| Electronic Structure of Primary Solid Solutions in Metals. By J. FRIEDEL, Centre de Recherches Metallurgiques de l'Ecole des Mines de Paris | 446 |

ADVANCES IN PHYSICS

A QUARTERLY SUPPLEMENT

of the

PHILOSOPHICAL MAGAZINE

VOLUME 3

OCTOBER 1954

NUMBER 12

Twinned Crystals

By R. W. CAHN

Department of Metallurgy, University of Birmingham
(temporarily at the Johns Hopkins University, Baltimore, Md., U.S.A.)

§ 1. THE NATURE OF TWINNING

1.1. *Definitions*

FOLLOWING Friedel (1926, p. 421), a twin may be defined as a polycrystalline edifice, built up of two or more homogeneous portions of the same crystal species in juxtaposition, and oriented with respect to each other according to well-defined laws.*

In this definition, the term *homogeneous* means that each portion can be referred to a single continuous lattice and that the constituent atoms are everywhere related in the same way to their nearest lattice points; less formally, each portion is a single crystal. *Juxtaposition* implies that the parts are in such intimate contact with each other over part of their bounding surfaces that they cohere, this cohesion being often, though not always, as strong as the internal cohesion of a single crystal. The requirement that the orientations be related according to well-defined laws is the most ambiguous part of the definition and has frequently given rise to dissension as to whether a particular specimen might justly be termed a twin.

Friedel (1926, p. 422) complained that "toute étude sérieuse du phénomène de macle [twin] se heurte à une masse énorme des faits erronés que le pitoyable abus de la bibliographie sans critique (Literatur) mélange inextricablement avec le nombre plus modeste des faits réels", and proposes that "macles d'imagination" be left out of account. Ambiguities arise mainly because natural minerals often consist of highly complex assemblies of crystals. If two constituent crystals have arisen

* A loose usage, current in metallurgical literature, when one of the homogeneous parts is larger than the others, is to refer to the smaller parts as being twins in the large crystal, which is sometimes called the 'parent grain'.

from independent nuclei, they will sometimes *by chance* be in approximate symmetry to each other with respect to a simple lattice element. By this is meant that the two crystals can be brought into one congruent orientation by reflection in a lattice plane of *low indices*, or by rotation through 60° , 90° , 120° or 180° about a lattice row of *low indices*. In a true twin the crystals must be accurately related in this way (but see rare exceptions, § 2.1.3.3), to within the error of goniometric or x-ray measurement, and the relation must be precisely reproduced in several samples to obviate the possibility that an observed relationship is due merely to chance meeting of independent individuals. Friedel was justified in restricting the designation *true twin* to an assembly obeying these two requirements, because it has been empirically determined that the second can only be satisfied if the first is. The 'erroneous facts' castigated by Friedel have crept into the literature owing to the practice of ignoring these requirements, particularly the second one.

A classification of twins according to their origin helps to emphasize the mutual dependence of the constituent crystals of a twin. We have three types:—

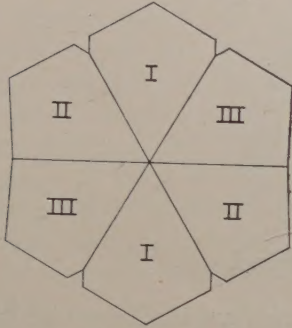
1.1.1. *Growth Twins*

Twinning arising in the course of a liquid-to-solid or vapour-to-solid phase change is common among minerals and artificial chemical compounds. In polycrystalline metals, the growth of one grain (crystal) at the expense of another may also lead to twinning. Twins so formed are termed *annealing twins*. The growing crystal makes a mistake, as it were, and some atoms are added in twinned orientation, which then continues to grow into a separate *individual*. Often this happens while the edifice is still minute. This is well illustrated by fig. 1, which is a drawing of a *repeated twin* in aragonite. (The expressive German term is *Vielling*.) The six individuals were all nucleated at the start at the centre and radiated from this point during the subsequent growth. Only three different *orientations* are present. The interface between a pair of sectors is also the symmetry plane relating their orientations. Because to casual inspection such an edifice appears to have a higher symmetry, it is also called a *mimetic twin*. When there are only two individuals, in contact along the twin symmetry plane, as in the spinel twin of fig. 4, we speak of a *contact twin*. If individuals related in this way occur alternately, we have *lamellar twinning*. Figure 3 is a drawing of lamellar twins in an etched section of recrystallized brass. The thick lines here represent boundaries between neighbouring grains whose orientations have no regular relationship, but the parallel-sided lamellae within each such grain are in twin relationship to the grain. In many minerals very fine lamellae occur in large numbers; this is known as *polysynthetic twinning*. Figure 2 is a drawing of a twin in fluorite; this type in which the interface follows a number of different planes or may be quite irregular, is called a *penetration twin*.

1.1.2. Thermal and Transformation Twins

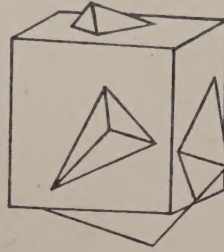
Phase transformations in the solid state are often accompanied by the formation of twins. These arise in two ways. When a crystal of the phase stable at low temperatures is heated, mechanical stresses may

Fig. 1



Repeated twin in aragonite.

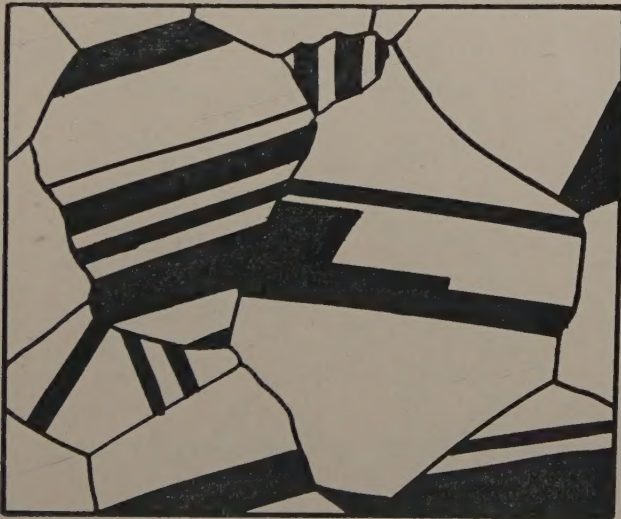
Fig. 2



Penetration twin in fluorite.

arise within it which cause twins to be generated. Such twins can be termed *thermal twins*, and are basically mechanical in nature. When a crystal of the high temperature phase is cooled through the transformation

Fig. 3

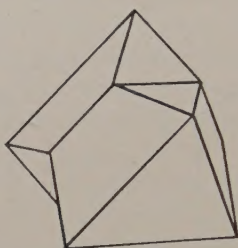


Annealing twins in a cross section of polycrystalline brass.

temperature, twins may again be formed in the low temperature phase. This is due to the fact that the transformation, on cooling, from a phase of high symmetry to one of lower symmetry, may involve cooperative atom movements in a nuclear region, which can take place in two or more ways.

The crystals generated by such alternative processes from an initial single crystal of the high temperature phase are then in twin relationship to each other. The twin-related crystals may or may not be lamellar.

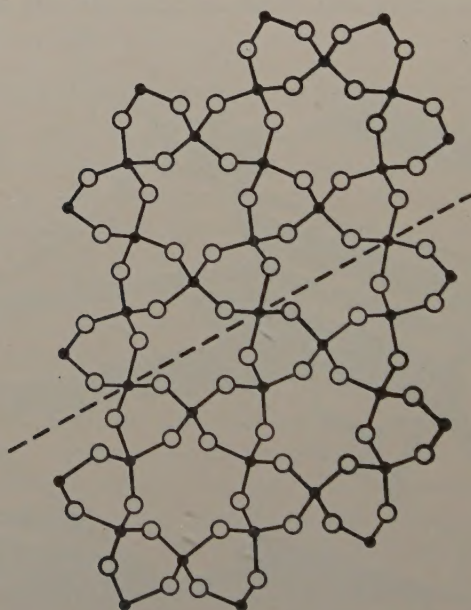
Fig. 4



Contact twin in spinel.

A good example of twins formed in this way are the Dauphiné (penetration) twins in quartz, which changes from a hexagonal to a trigonal symmetry during cooling. Figure 5 shows the internal structure of both

Fig. 5



Approximate projection on (0001) of the atomic structure of a Dauphiné twin in quartz. The dashed line is the twin interface. Solid circles represent Si atoms, open circles, O atoms.

individuals of such a twin; the hexagonal 'stars' of silicon and oxygen of the high temperature form can still be recognized in distorted form.

1.1.3. Mechanical Twinning

Cooperative atom movements in phase transformations may extend over quite large volumes of crystals. When this happens, the transformation is termed *martensitic* (from Martens, who discovered the first transformation of this type in carbon steel). If the atom movements in a crystal results in a new crystal of different orientation, but identical structure, the process is termed mechanical twinning. That part of the parent crystal which is thus transformed undergoes a macroscopic change of shape which can be described exactly as a simple shear. An array of points (in this case a lattice) is said to undergo a simple shear if each point moves parallel to a certain direction (the shear direction) through a distance proportional to the distance of the point from a particular plane (the interface). Points on the wrong side of the interface do not move and are not transformed to the new orientation. It is an empirical fact that mechanically induced twinning always occurs in this way, with one exception (piezocrescence in quartz, § 3.4).

The interdependence of the crystals constituting a twin is particularly clear in the case of a mechanical twin, because the starting condition is a single crystal.

1.1.4. Previous Reviews

The external morphology and classification of growth twins is treated in many mineralogical textbooks (e.g., Dana and Ford 1932). Friedel's (1904, 1926) classic treatment is centred on consideration of the lattice. Unfortunately Friedel's views on the dangers of bibliographies precluded him from giving any references in his otherwise most useful books. An excellent historical review of the stormy debates among crystallographers as to the correct formal description of twins has been collated by Löffler (1934). Concise treatments of the formal lattice geometry of twins are being published by Donnay (1954) and by Donnay and Donnay (1954). Recently, structural considerations have entered into the discussion of growth twins (Buerger 1945, Hartman 1953). Facts about annealing twins have been reviewed by Burke and Turnbull (1953).

Transformation twinning has not been widely studied as yet. Some of the basic principles are reviewed by Buerger (1951) and by Ubbelohde and Woodward (1947).

The geometry of mechanical twinning has been systematized by Johnsen (1914), Schmid and Boas (1935) and Tertsch (1949). Experimental information has been collected by Mathewson (1928), Barrett (1952), Clark and Craig (1953) and Hall (1954) for metals, and by Tertsch (1949) for minerals. The extensive Russian work in this field has recently been reviewed by Cahn (1953 c). The present article is an attempt at a critical review of facts and theories on twinning for metals and non-metals indifferently.

1.2. Formal Crystallography of Twinning

Two empirical facts are central to the crystallography of twins, of whatever origin. One is, that a pair of crystals, or *individuals*, which are in twin relation possess an element of macroscopic symmetry over and above that which either component crystal possesses by itself. The other fact is that this extra symmetry must be of the kind encountered in crystal morphology—i.e., a centre of symmetry, a plane of symmetry, or a rotation axis of 2, 3, 4 or 6-fold symmetry. If the extra symmetry element is a plane of symmetry (*twin plane* for short), it must be parallel to a lattice plane in both crystals; if an axis of symmetry, it must be parallel to a lattice row common to both crystals. If a twin contains individuals in more than two orientations (repeated twin), then these are related *in pairs* by distinct symmetry elements of the types referred to. An observed twin with a particular symmetry element establishes a *twin law* for the substance in question. A single substance can have several twin laws and often does.

There is an alternative, elaborate system of describing twins (expressed in different terms by diverse mineralogists, but usually associated with the name of Tschermak), which brings in symmetry planes and axes which are not parallel to lattice planes and rows. Since, however, no unambiguous instances of such twin laws have been discovered, we follow Friedel in rejecting them as being unsubstantiated. Friedel's classification is, then, the simplest and clearest available.

The extra symmetry of the twin is purely macroscopic. The internal structure of each component crystal is just the same as it would be for a single crystal in isolation, except in the immediate vicinity of the interface between the two crystals. This local disturbance is, however, of central importance in determining whether a twin law which is *a priori* possible is actually observed.

1.2.1. Friedel's Rules

We shall explain these rules in some detail, since no full exposition in the English language exists. All known twins fall into one of the four categories defined by these rules, with a very few exceptions (for which, see § 2.1.3.3).

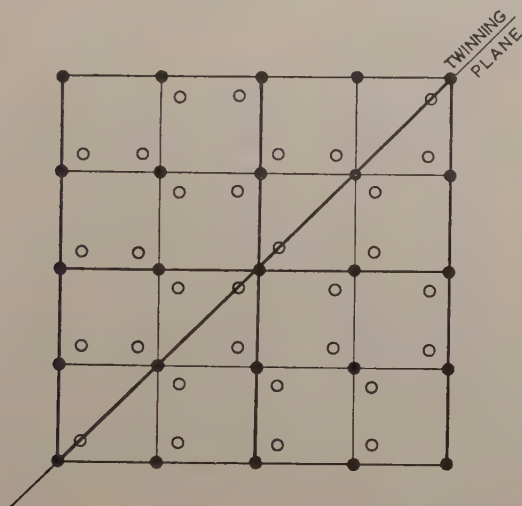
Romé de l'Isle (1783) was the first to describe twins in his account of the mineral staurolite—twins which are still being studied today. His pupil Haüy (1801) made angular measurements on staurolite twins by contact goniometry, and observed that any face of one individual has a face of the other individual parallel to it.

Friedel's method of describing and classifying twins stems from this observation. If Haüy's rule is exact, it implies that the *lattices* of the two individuals are exactly parallel to each other. This corresponds to the first of the four types of twin in Friedel's classification:—

1.2.1.1. *Twinning by Merohedry*.—This concept is due to Bravais. The term merohedry, of Greek origin, implies that each component

crystal has fewer faces than it would have if the structure had the highest symmetry possible for the lattice on which it is based. Thus the merohedral species, pyrite, is cubic but belongs to the class $(2/m) \bar{3}$, while its lattice, which always possesses the highest symmetry possible for the corresponding crystal system, has the symmetry $(4/m) \bar{3} (2/m)$. The lattice therefore possesses a plane of symmetry parallel to (110), but the structure does not. Pyrite is often found twinned with respect to a (110) symmetry plane, in the form of contact or more usually penetration twins. Figure 6 illustrates the structure of a contact twin. Since the angular positions of all faces is determined by the lattice and not by the arrangement of atoms with respect to the lattice, Haüy's rule follows as a corollary.

Fig. 6



Atomic structure of a contact twin in pyrite, projected on (001).

Dauphiné twinning in quartz is another example of twinning by merohedry.

The second of Friedel's four twin types is:—

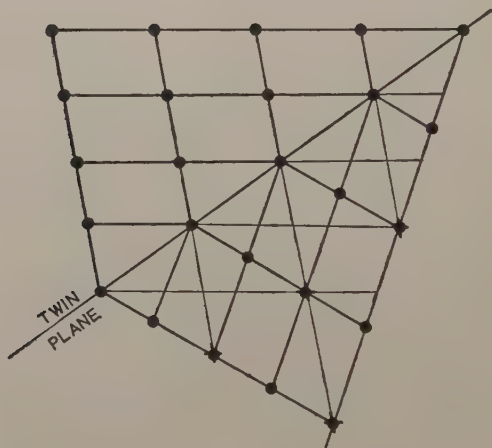
1.2.1.2. *Twinning by Reticular (or Lattice) Merohedry.*—Here the lattices of the two individuals are not in parallel orientation, but a small multiple lattice exists which continues without disturbance from one individual to the other (fig. 7). In other terms, a fraction of the lattice points in each individual form a single continuous lattice of their own, today sometimes called the *lattice of coincidence sites*, or *simply coincidence lattice* (Kronberg and Wilson 1949). The reciprocal of this fraction is called the *twin index*.

This type of twinning is mainly restricted to cubic crystals. In systems of low symmetry it is only possible if axial ratios and interaxial

angles happen to have particular values (Donnay and Donnay 1954). The growth twins in galena, fluorite, diamond, silicon and germanium, the annealing twins in brass, and the mechanical twins in iron and molybdenum, are all of this type. These all have (111) as contact plane, except iron and molybdenum, which have (112). Either of these can be quoted as twin *symmetry* plane for any of these substances, for the final result is the same.

The term 'reticular merohedry' is applied to this kind of twinning because the coincidence lattice possesses one or more symmetry elements that the lattices of the individuals do not possess. However, the lattice and the structure of each individual possesses other symmetry elements which are not shared by the coincidence lattice—here is a distinction from the preceding case. Thus in the case of an annealing twin in brass

Fig. 7



To illustrate reticular merohedry.

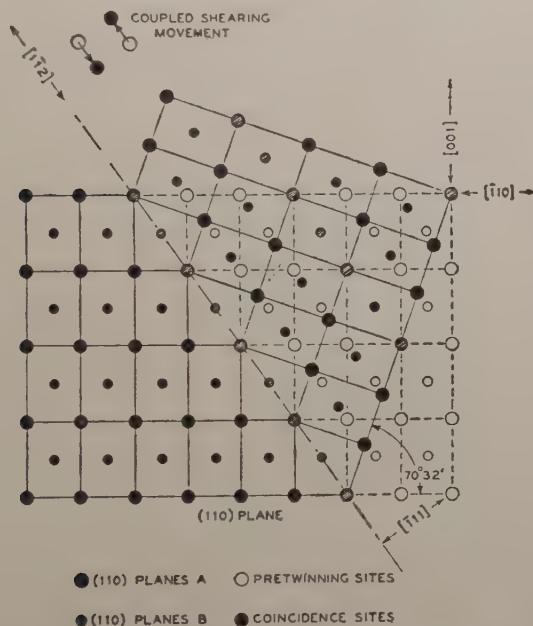
with contact plane parallel to (111), the coincidence lattice has symmetry planes parallel to (111), $(11\bar{2})$, $(\bar{2}11)$ and $(1\bar{2}1)$. These are not, of course, symmetry planes in the face centred cubic lattice—they could not be twin planes if they were. However, the coincidence lattice does not have four-fold symmetry, while the face-centred cubic lattice does.

These points become clear on inspection of fig. 8, which is taken from a paper by Ellis and Treuting (1951). The identity between Ellis and Treuting's approach and that of Friedel was pointed out by Whitwham, Mouflard and Lacombe (1951).

Another instance of twinning by reticular merohedry is found in zinc blende, which has a low structure symmetry ($\bar{4}3m$). Here the extra symmetry element of the twin is a two-fold twin axis parallel to $[111]$ (cf. § 1.3.1.2).

1.2.1.3. *Twining by Pseudo-Merohedry*.—This concept is due to Mallard. This, the third of Friedel's twin types, is an extension of the first. Instead of possessing a symmetry element which the structure does not possess, the lattice of each individual only possesses extra elements of *pseudo-symmetry*. This is exemplified in fig. 9(a), which refers to an imaginary substance. For simplicity we suppose all other atoms to be directly above or below those drawn. Then the plane normal to the paper and passing through AD is a plane of pseudo-symmetry. Also the lattice rows AB, AC are axes of two-fold pseudo-symmetry. In fact, the lattice is *nearly* orthorhombic.

Fig. 8

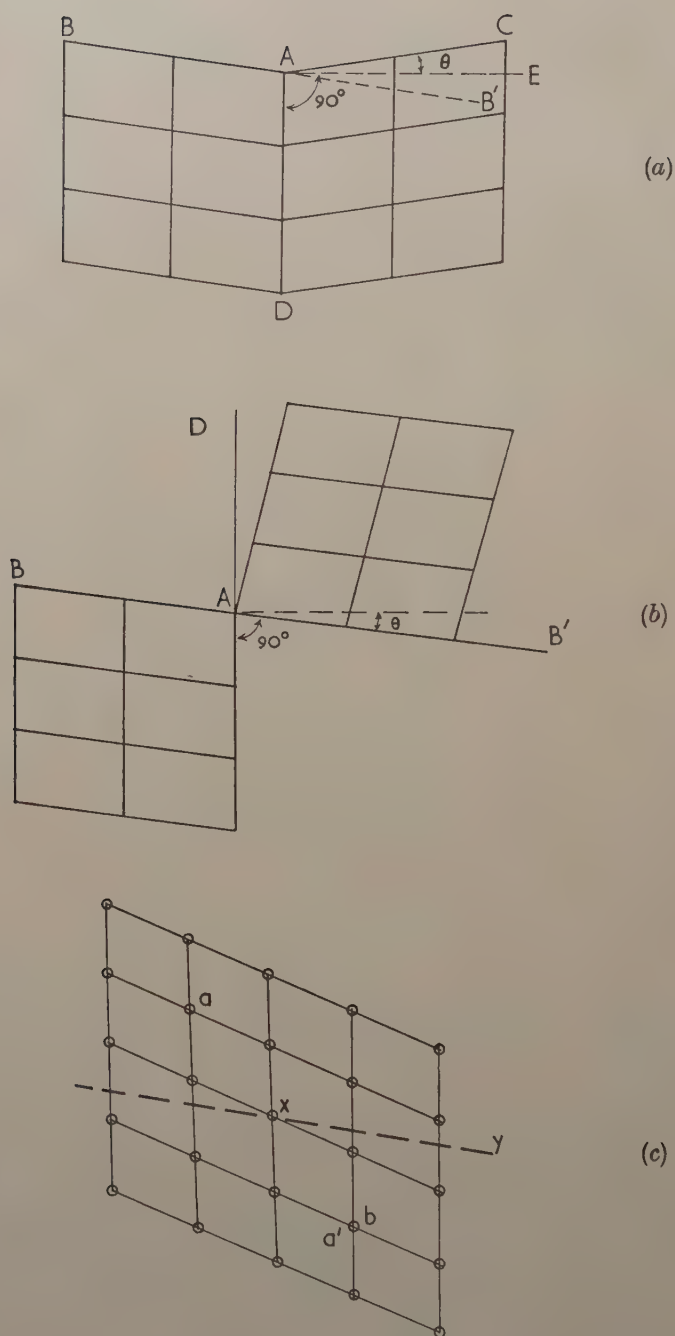


Atomic structure of a twin in a face-centred cubic element, projected on $(1\bar{1}0)$. The twin and contact plane is (111) . (From Ellis and Treuting 1951.)

It is found empirically (Mallard's Law) that all twins of this type can be accurately described in terms of a twin plane parallel to a *lattice plane* which is almost a symmetry plane of the lattice, or in terms of a twin axis parallel to a *lattice row* which is almost a symmetry axis of the crystal structure. The two alternatives are not identical. Figure 9(a) shows a twin with a twin plane, through AD, while fig. 9(b) shows one with a twin axis parallel to AB. The two kinds are often distinguished as *reflection* and *rotation twins* respectively.

The angle CAB' is a convenient measure of the pseudo-symmetry of the structure. Half this angle (CAE) is called the *obliquity* of the twin.

Fig. 9



Reticular pseudo-merohedry. (a) Reflection twin, (b) rotation twin, (c) derivation of rhombic section.

Strictly defined, this is the angle between the normal to that lattice plane which is a pseudo-symmetry plane, and the lattice row which is a pseudo-symmetry axis. The obliquity is always smaller than shown in fig. 9; it rarely exceeds 5° , and is often $1-2^\circ$.

Haüy's rule is not strictly obeyed for twins by pseudo-merohedry; faces on the two individuals will only be roughly parallel, the deviation ranging from zero to twice the obliquity. Ironically, Haüy's observation on staurolite, which prepared the way for the recognition of twins by (strict) merohedry, is not accurately correct, for staurolite twins are now known to be of pseudo-merohedral type. The obliquity is only $1^\circ 16'$, and the correspondingly small angles between faces must have been missed by Haüy's crude contact goniometer. Staurolite has actually two twin laws:—(i) with a threefold twin axis $[101]$, (ii) with a four-fold twin axis $[100]$ (Friedel 1922, Hearst, private communication). This is unusual, though not unique. It is far more common to encounter two-fold twin axes, or twin planes.

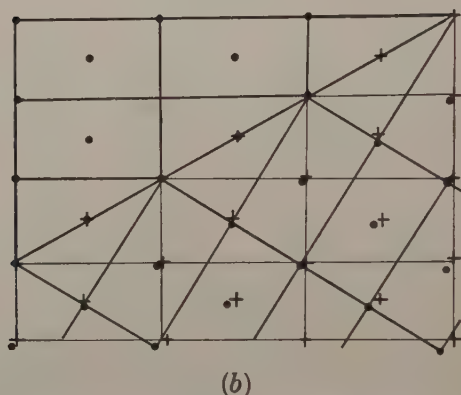
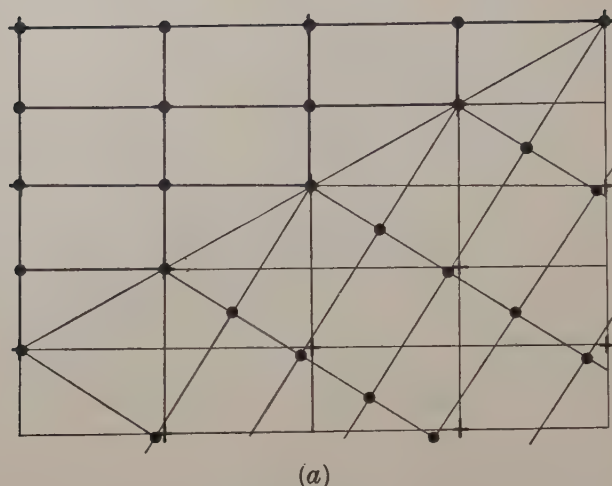
Twins by pseudo-merohedry are legion among minerals and artificial compounds (cf. in particular Friedel's texts). We will mention only the most famous, the albite twins. Albite is a triclinic feldspar, pseudo-monoclinic, since the b axis is almost normal to the a and c axes. Therefore (010) is a pseudo-symmetry plane and $[010]$ a pseudo-symmetry axis. Twins with a (010) twin plane (Albite Law) and with a $[010]$ twin axis (Pericline Law) are both widespread. The obliquity is $3^\circ 36'$.

1.2.1.4. *Twinning by Reticular Pseudo-Merohedry.*—This kind of twinning bears the same relation to twinning by strict reticular merohedry, as twinning by pseudo-merohedry bears to that by strict merohedry. Here it is a small *multiple* lattice which has pseudo-symmetry, and the points of this multiple lattice in one individual, when prolonged into the other, conicide *approximately* with the points of a multiple lattice in the latter. As in the case of pseudo-merohedry, the disregistry rapidly increases away from the interface.

An example is aragonite (CaCO_3), which is the orthorhombic polymorph of calcite. Orthorhombic crystals have pseudo-symmetry planes, namely (110) and $(1\bar{1}0)$, if the axial ratio a/b approximates to unity, but in fact it is more common to find a^2/b^2 approaching unity. Then the angle $(110)-(1\bar{1}0) \sim 60^\circ$. In aragonite this angle is $63^\circ 48'$, and morphologically the crystal is pseudo-hexagonal. The pseudo-symmetry plane (110) acts as twin plane; contact, polysynthetic, repeated and thermal twins are observed. Such (110) reflection twins in pseudo-hexagonal orthorhombic minerals are widespread.

The reason why aragonite comes under the heading of reticular rather than simple pseudo-merohedry is that its lattice is not C-face centred (fig. 10 (a)). If it were (fig. 10 (b)), then the crystal lattice itself, and not just a multiple of it, would be pseudo-hexagonal.

Fig. 10



Twins of pseudo-hexagonal lattices. (a) Primitive, (b) C-face centred.

1.2.2. Mechanical Twins

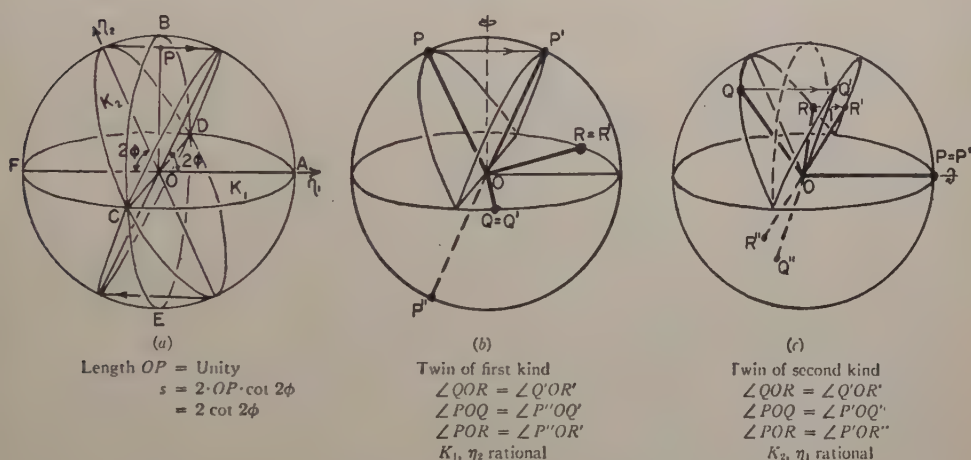
A full treatment of the formal crystallography of mechanical twinning was first published by Johnsen (1914). The following treatment is based upon Johnsen's, but some new points are brought into consideration. Since a mechanical twin is always formed by a macroscopically homogeneous shear, the crystal lattice will be progressively distorted from its original shape as the shear is attained. Our treatment is intended to show under what circumstances this requirement will be satisfied. Individual atoms of the structure generally need to execute small motions in addition to the macroscopically observed shear if the original crystal structure is to be restored, even if the lattice itself is restored by the shear alone. This is true *a fortiori* if a multiple lattice only is restored.

Figure 11 (from Cahn 1953 a) represents a sphere cut from a single crystal. K_1 is a central section of the sphere which for the moment we will

call the *plane of gliding*.* Each point above K_1 moves parallel to the glide direction η_1 , through a distance proportional to its height above K_1 . The constant of proportionality s is called the *magnitude of shear*. The plane through η_1 normal to K_1 is the *plane of shear*. K_2 is the only central section of the sphere besides K_1 which remains circular after twinning. K_1 and K_2 are inclined at an angle 2ϕ , defined by the equation $s = 2 \cot 2\phi$. K_2 and the plane of shear intersect in a line designated η_2 . The twinning operation distorts the sphere into an ellipsoid, whose major axis is inclined to η_1 at angle ϕ .

We now show that there are two ways in which we can choose three lattice row lines which will have the same periodicity and mutual inclination before and after twinning. (A *lattice row line* is the vector joining a lattice point to that lattice point which is taken as origin.) This is

Fig. 11



The elements of a mechanical twin. (From Cahn 1953 a.)

equivalent to choosing three radii of the sphere, parallel to lattice rows, which remain unaltered in length and mutual inclination after twinning.

1.2.2.1. *Twinning of the First Kind*.—Since K_1 and K_2 both remain circular sections, all radii lying in either of these planes are unchanged in length after twinning. Let K_1 be parallel to a lattice plane and let OQ , OR be parallel to two arbitrarily selected lattice rows lying in that plane.

* Following mineralogical usage, *glide* is taken as a comprehensive term. If some adjacent lattice planes move parallel to a lattice row through an integral multiple of the lattice periodicity along that row, we have *translation* (mineralogical term) or *slip* (metallurgical term). If each pair of adjacent planes moves through the same relative distance, and this is a fraction of the periodicity in the glide direction, we have *mechanical twinning*. The term *glide* does not cover martensitic phase transformations, which involve more complex lattice distortions.

Let η_2 ($=OP$) be parallel to a lattice row. Not only is this radius unaltered in length, but the angles it makes with the other two vectors are unaltered; this would not be so if we had taken OP to be any other radius in the plane K_2 . This statement is only exact if we measure the angles after twinning from OP'' instead of from OP' , but this is permissible because all lattices have centres of symmetry. OQ and OR are not affected by the twinning shear, and consequently our three radii remain unaltered in length and mutual inclination. When K_1 is a lattice plane and η_2 a lattice row, we have twinning of the *first kind*. K_2 and η_1 need not be parallel to lattice elements, i.e., they can be *irrational*.

1.2.2.2. *Twinning of the Second Kind*.—Now let K_2 be parallel to a lattice plane, and let OQ and OR again be parallel to two lattice rows in that plane. Let η_1 ($=OP$) be parallel to a lattice row. By similar arguments it is again found that these three radii maintain the same lengths and inclinations after shear. This is the case of twinning of the *second kind*. K_1 and η_2 can be irrational.

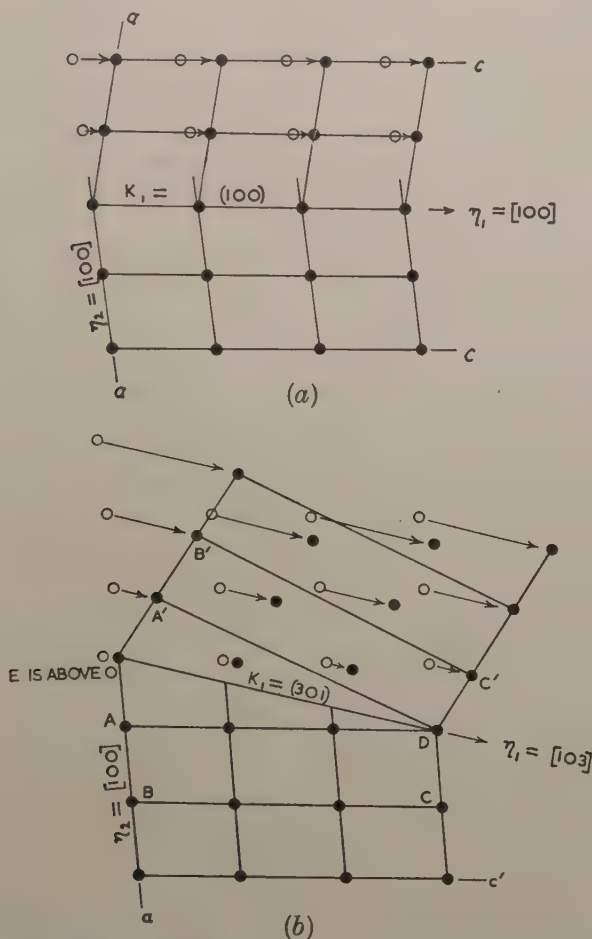
When a crystal has high symmetry, it is often found that K_1 , K_2 , η_1 and η_2 are all parallel to lattice elements. Twins for which this is true have been termed *compound twins* (Cahn 1953 a). Such twins are the rule among metals, but the exception in the realm of minerals.

1.2.2.3. *Lattice Changes in Mechanical Twinning*.—We have shown that, if K_1 and η_2 , or K_2 and η_1 , are lattice elements, three lattice row lines can be found which are unaltered in length and mutual inclination after the lattice has been sheared. This is equivalent to saying that the original lattice is restored by the shear, *if* these three row lines define a unit cell of the lattice. For centred lattices this is a cell having lattice points at the corners only. If any of the three row lines is not parallel to a side of a unit cell, then the shear restores a multiple of the original lattice, which may or may not itself be restored. Figure 12 (a) illustrates this. Here $K_1=(100)$ and $\eta_2=[100]$. η_1 is in the plane of the figure, for simplicity. The lattice is restored by the shear. In fig. 12 (b) η_2 is still $[100]$ but $K_1=(\bar{3}01)$. The three invariant row lines are now OA , OD , OE , among which OD is not a side of a unit cell. The multiple lattice $ABCD$ is restored but not the simple lattice. On the other hand if K_1 were $(\bar{2}01)$, both the multiple lattice and the simple lattice would be restored.

Johnsen (1916 a and b, 1917) and Grünh and Johnsen (1917 b), have discussed the general conditions for a primitive or centred lattice to be restored (cf. also Schmid and Boas 1935, p. 78). They also postulated that the capacity of a lattice to be restored ('Schiebungsfähigkeit') was a necessary condition for twinning to be possible at all, for, they argued, if the lattice could not be restored, *a fortiori* the structure could not. Now that many crystal structures have been determined, this postulate is known to be wrong. Thus the twin law for mechanical twins in tin is $K_1=(301)$, $\eta_2=[101]$, and the lattice of tin is not restored by this shear. Yet this

twin law is observed even though a different choice of twin law would have allowed the lattice to be restored. The restoration of a multiple lattice appears to suffice. What this implies in terms of the motions of individual atoms is discussed in § 1.3.2.

Fig. 12



Restoration of lattices by twinning. Triclinic primitive lattice, projected into the (010) plane. (a) $K_1 = (100)$, $\eta_2 = [100]$; the lattice is restored. (b) $K_1 = (301)$, $\eta_2 = [100]$; the lattice is not restored, but a multiple lattice is.

There is no apparent relationship between the capacity or incapacity of a lattice to be restored by shear, and the classification of the twin law under Friedel's scheme. An obvious rule is that a twin by merohedry cannot be achieved mechanically, if we except the abnormal phenomenon of piezocrescence in quartz (§ 3.4). Also there is a clear relation between

Friedel's twins by pseudo-merohedry or reticular pseudo-merohedry, and reciprocal mechanical twin laws. If the lattice plane of pseudo-symmetry is K_1 , the pseudo-symmetry axis which is almost normal to it serves as η_2 ; in the reciprocal law, the axis serves as η_1 , and the pseudo-symmetry plane as K_2 . The angle 2ϕ in fig. 11 is the complement of the angle of obliquity CAE (fig. 9).

The orientation relationships that result from mechanical twinning can be seen by inspecting fig. 11. In twinning of the first kind, the two individuals are related by symmetry in K_1 , which is therefore the twin plane as well as being the plane of glide. In twinning of the second kind, η_1 is the two-fold twinning axis. These relationships have been many times confirmed, by examination in polarized light in the case of minerals and by x-ray diffraction in the case of metals (e.g., Johnsen 1907, Cahn 1953 a, Kelly 1953).

Mügge (1894) was the first to discover that if a substance could be twinned mechanically according to a twin law of the first kind with $K_1=(hkl)$, $\eta_2=[UVW]$ it might also possess a twin law of the second kind with $K_2=(hkl)$, $\eta_1=[UVW]$. He discovered this in $\text{BaCdCl}_4 \cdot 4\text{H}_2\text{O}$ (triclinic), for which (i) $K_1=(010)$, $\eta_2=[010]$; (ii) $K_2=(010)$, $\eta_1=[010]$, and termed the two twin laws 'reziproke Zwillinge' (*reciprocal twins*). Friedel's term is 'macles correspondants'. Such paired twin laws are now known to be common among minerals and a pair has been observed in orthorhombic uranium (Cahn 1953 a). They are unusual in highly symmetrical structures, but have been observed, for instance in cubic lead sulphide (Seifert 1928).

Johnsen (1916 a) proved generally that if a particular twin law produced restoration of the lattice, then the reciprocal twin law had the same property. From this it can be intuitively concluded that the *atom* motions associated with two reciprocal twin laws, whether or not the lattice is restored in them, are closely related to each other.

The crystallographic formulae for calculating the new indices of natural faces or lattice planes after mechanical twinning have been published elsewhere (Schmid and Boas 1935, Tertsch 1949) and need not be repeated here.

1.3. *Relation of Twinning to Crystal Structure*

Our treatment of twin crystallography up to this point has only been concerned with the lattices of the component crystal, and not with the position of the atoms themselves. Friedel's rules and the formal description of mechanical twins of the first and second kinds provide us with sets of conditions empirically found to be *necessary* for twinning to occur, but they are certainly not sufficient. The total number of species found capable of twinning, though large, is minute compared with the number of identified crystal species, and yet many of these species must have some lattice planes or axes of reasonably low indices which are also pseudo-symmetry elements and could in principle serve as twinning

elements. Many twin laws by merohedry are possible for cubic crystals, and if the restoration of a multiple lattice is sufficient, the number of the mechanical twin laws which are *a priori* possible is almost infinite. The purpose of bringing the crystal structure into the discussion is to seek further conditions necessary for twinning to occur.

1.3.1. *Structural Disturbance at Twin Boundaries*

For growth twins and mechanical twins alike, one would expect the state of disturbance of the crystal structure at the interface between the components to be particularly slight in the substances in which twins can in fact be obtained. In the comparatively few cases which have been examined from this point of view, this supposition has been verified. Generally, it is found that a fraction of the atoms at the interface have the same immediate coordination as they have in the normal structure, though the second nearest neighbours are usually arranged differently. Attention has been largely restricted to contact twins as distinct from penetration twins (for which cf. § 2.1.1).

1.3.1.1. *Elements*.—Mathewson (1928) appears to have been the first to make such an investigation. He examined the structure of interfaces of growth twins in face-centred cubic metals such as copper, and of mechanical twins in close-packed hexagonal metals such as zinc. In the former case the interface coincides with a plane of atoms parallel to (111) in each component. Each atom in this plane is surrounded by twelve other atoms all at the same distance as the nearest neighbours in the normal crystal structure, but they no longer fall at the apices of a regular dodecahedron. In fact, for a distance equal to the height of one hexagonal unit cell, the structure has become close-packed hexagonal. The second nearest neighbours are closer together in the close-packed hexagonal than in the face-centred cubic, and so the second-nearest neighbours of atoms at the interface are abnormally close. A similar situation exists at the (112) interface of a twin in iron.

McKeehan (1927) and Preston (1927) have examined in detail the relative distortions at interfaces parallel to (111) or (112) in face- and body-centred cubic twins. They concluded that (111) involves the lesser distortion for face-centred cubic metals, and (112), for body-centred. In agreement with this, the many spontaneously formed annealing twins in face-centred cubic metals always have interfaces parallel to (111), while in iron (112) interfaces are found not only in mechanical twins but also in crystal pairs artificially prepared in twin relation; attempts to force twin interfaces in iron to adopt a (111) orientation failed (Dunn, Daniels and Bolton 1950).

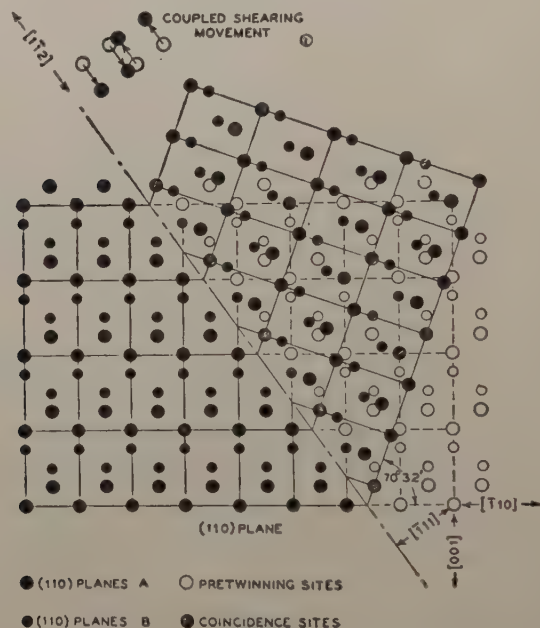
Aminoff and Broomé (1931) and Ellis and Treuting (1951) showed that for the diamond cubic structure, if the position of the interface is properly chosen (fig. 13) the four nearest neighbours of any of the atoms immediately adjacent to the interface (which does not itself contain any atoms) are not only at the normal distances but are still at the apices

of a regular tetrahedron. It follows that second-nearest neighbours are also at the normal distance, though their positions are abnormal.

In the case of mechanical twins in hexagonal close-packed metals (twin plane $\{10\bar{1}2\}$), the mean interatomic distances for first nearest neighbours depend on the exact position chosen for the twin interface relative to the atom sites.

The writer (Cahn 1953 a) has examined two twin laws in uranium from a structural point of view. In neither cases is the distortion notably great, but the smoothness of the transition layer is especially noteworthy in the case of the law with $[312]$ as twin axis, for here the interface is not parallel to a lattice plane.

Fig. 13



Atomic structure of a twin in diamond, projected on $(1\bar{1}0)$. The twin and contact plane is (111) . (From Ellis and Treuting 1951.)

1.3.1.2. *Zinc Blende*.—In their pioneering paper, Aminoff and Broomé (1931) also examined twin interfaces in the cubic form of zinc blende, ZnS , and in galena, PbS , which is also cubic.

Zinc blende consists of two interpenetrating face-centred cubic lattices possessing respectively zinc and sulphur atoms at the lattice points. The structure is identical with that of diamond, if half the carbon atoms are replaced by zinc and the remainder by sulphur. The result of this substitution is that zinc blende, unlike diamond, has no centre symmetry. Though the interface of zinc blende twins is parallel to (111) , it is found that the polar $[111]$ directions of the two individuals are parallel, hence (111) cannot be a twin plane. The twin is defined by a 180° rotation about

[111] as twin axis. Aminoff and Broomé showed that this twin law implied the presence of a cell possessing the wurtzite structure at the interface. This hexagonal structure is a polymorphic form of ZnS , stable at low temperatures (the cubic form is metastable at room temperature). As in diamond, the first and second nearest neighbours are at their normal distances, but the second nearest neighbours are arranged abnormally. If the twin were to have (111) as twin plane (i.e. if the polar directions were reversed), the transition structure would be different and only nearest neighbours would be at the correct distance. The possibilities are illustrated in fig. 14. The above conclusions hold, irrespective of the positions of the interface relative to the atomic sites.

1.3.1.3. *Galena*.— PbS crystallizes in the rocksalt structure. Mechanical twins form on many different planes (Seifert 1928) (cf. § 1.3.4) but growth twins all have twin plane and contact plane parallel to (111). The second-nearest neighbour distance is altered, but again a unit cell of a distinct structure type (the NiAs structure) occupies the neighbourhood of the twin interface. PbS itself never crystallizes in this structure, but another sulphide, FeS , does so. Compare here the close-packed hexagonal structure of the interface of annealing twins in copper. Copper has no stable hexagonal modification, but the similar metal cobalt has both cubic and hexagonal forms.

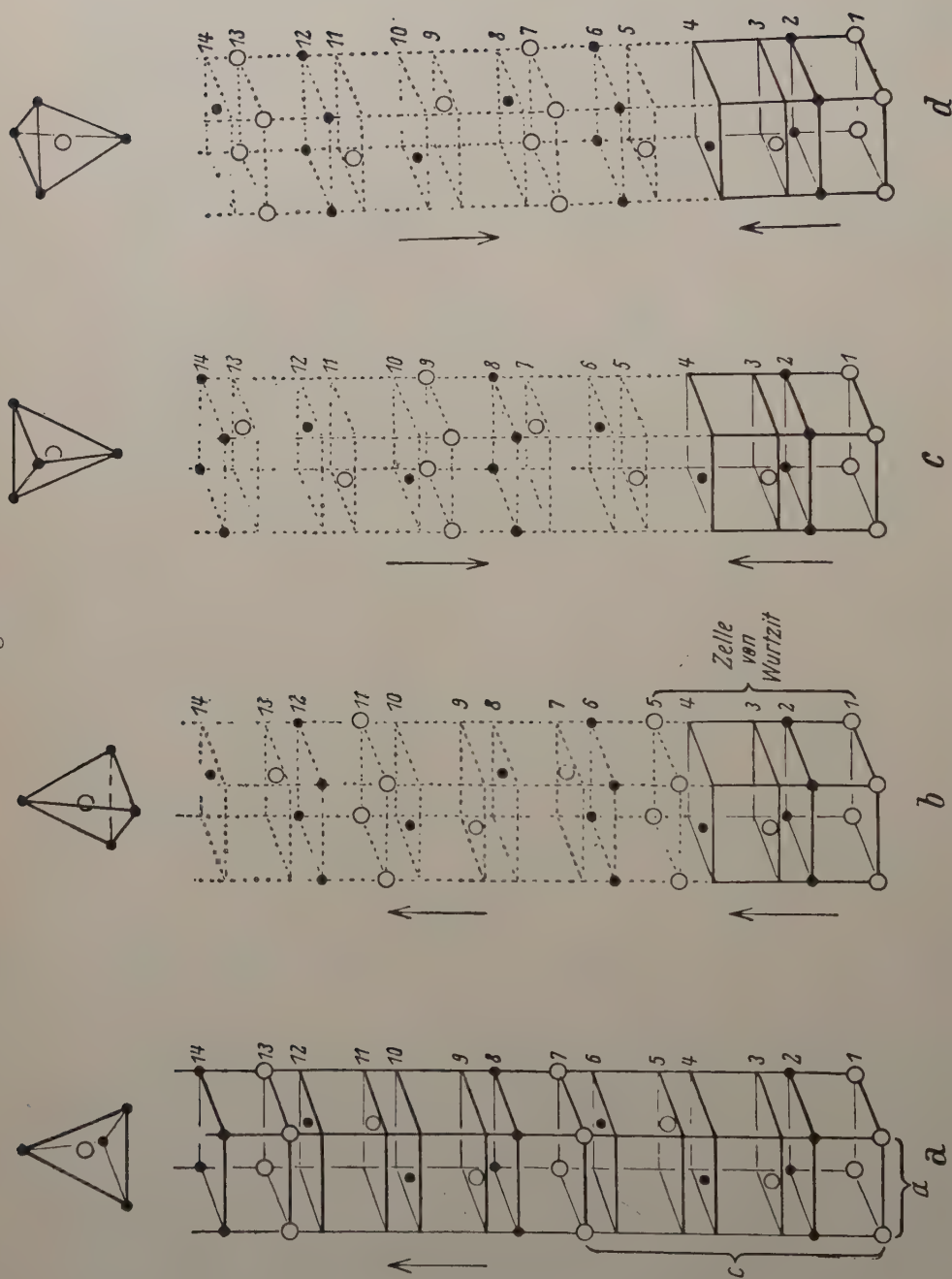
All the examples quoted up to now confirm two general rules proposed by Aminoff and Broomé :—

1.3.1.4. *Aminoff and Broomé's Rules*.—1. When two individuals form a contact twin either one or two layers of the structure at the interface are common to both individuals.

2. The atomic coordination in the transition layer is either identical with that in the crystal structure (diamond) or closely related to it. In the latter case, the transition structure is that of a possible polymorphic modification of the structure, or else that of a modification which would be plausible for that substance.

1.3.1.5. *Felspars*.—The first of these laws applies to such other twin laws in more complicated structures as have been structurally examined. The most striking example is the structural study of twinning in the feldspars by W. H. Taylor (1933) and Taylor, Darbyshire and Strunz (1934) (cf. also the concise account in Bragg 1937). For all five common twin laws in orthoclase (monoclinic) and albite (triclinic) the linking array of oxygen tetrahedra surrounding silicon and aluminium atoms continues unchecked, and almost undistorted, across the interface. For the 'Baveno' law (twin plane (021)), the structures have to be fitted together after a relative displacement along the twin plane, which thus becomes a glide plane of symmetry (in the sense used in space group theory). This is permissible for a growth twin but must cause severe stresses in the interface of a mechanical twin.

Fig. 14



Atomic structure of zinc blende. The layers are parallel to (111) . (a) Normal untwinned structure (a and c are repeat distances along $[110]$ and $[111]$); (b) rotation twin about $[111]$, as observed in nature; (c) hypothetical twin by combined reflection and rotation; (d) hypothetical reflection twin. — The arrows indicate the sense of the polar axis. (From Aminoff and Rasmus 1933)

1.3.1.6. *Aragonite and Calcite*.—For contact twins on (110) in aragonite, the orthorhombic modification of CaCO_3 , Bragg (1937) has shown that there is a transition structure which could belong to either individual. Donnay (private communication) has pointed out that Bragg's drawing of an aragonite twin is based on the implicit assumption that the twin plane is again a glide plane of symmetry (with a glide of $c/2$). Yet aragonite undergoes 'mechanical twinning' by shear when heated, though never through mechanical stressing alone. In addition to executing the normal shear in the $[1\bar{1}0]$ direction, each lattice point must undergo a sudden glide of $c/2$ as the interface passes it.

Calcite, the rhombohedral form of CaCO_3 , can readily be twinned by applied stress, with $(01\bar{1}2)$ as twin plane. Friedel (1926, p. 465) has analysed the structural aspects of this twin law. The Ca and C atoms are brought to their correct positions by the twinning shear; only the oxygen groups have to rotate about the C atoms which they surround. Bragg's drawing shows that this is also approximately true for aragonite, the $c/2$ glide apart. It seems then that it is this glide (which distinguishes the aragonite twin from other mechanical twins) which must be held responsible for the difference in the ease of twinning in the two cases (cf. also § 1.3.2.1).

In calcite the CO_3^- groups are parallel to the twinning plane. This was also established for several of the complex cyanides such as $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, which twin very easily (Brasseur and de Rassenfosse 1941). No detailed analysis of the twin interface was made.

1.3.1.7. *Pseudobrookite*.—Von Glazecynski (1948) studied the structure of twins in pseudobrookite, Fe_2TiO_5 (orthorhombic). Three contact twin laws with twin planes (210), (230) and (430) are well established. For all these, an almost undisturbed continuity of the network of oxygen octahedra exists across the interface. Von Glazecynski goes so far as to propose that the existence of such good continuity shall serve as criterion whether a specimen is a genuine twin when difficulties of measurement make this morphologically uncertain. Some 'imaginary' twin laws were also found in this mineral. The angular relationships here are not strictly reproducible; these intergrowths are apparently caused by epitaxial deposition of anatase (TiO_2) on which more pseudobrookite is deposited in a new orientation.

1.3.1.8. *Pyrite*.—Von Glazecynski (1950) has also studied the structure of the (110) contact twin law in pyrite (a twin by strict merohedry), and has concluded that the sulphur network is not much distorted when the interface is parallel to (110).

1.3.1.9. *Quartz*.—Bragg (1937) mentions that the twin law in quartz with $(11\bar{2}2)$ as twin plane allows considerable linking of the silicate tetrahedra across the interface. The penetration twins according to the Dauphiné law have virtually no strain at the interface; this was shown by means of a sensitive x-ray method by Bond and Andrus (1952).

It is no doubt due to the near continuity of structure across the interface (cf. fig. 5).

1.3.2. *Atom Movements in Mechanical Twinning*

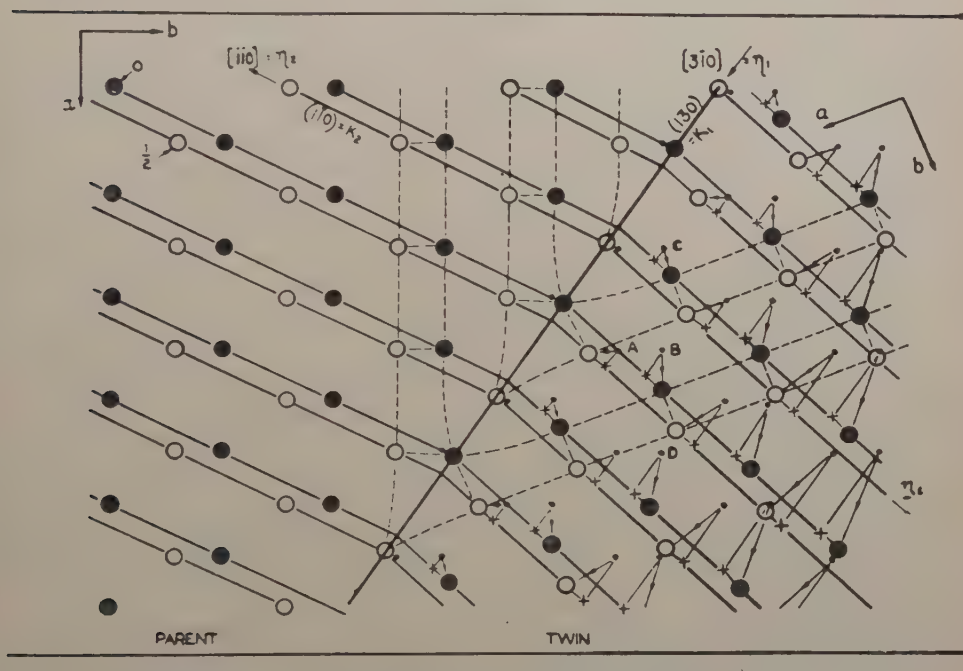
As we have seen in 1.2.2, the empirical crystallography of twinning tells us only that the lattice, or a multiple thereof, is restored after twinning. *Unless* (i) the atoms of the structure are all of one kind and all located at lattice points, and (ii) the lattice itself (not merely a multiple) is restored, the atoms will not all be in the correct positions after the twinning shear is completed. This has been recognized and discussed by Friedel (1926, p. 465) for the case of calcite, Mathewson (1928) for zinc, Barrett (1948) for magnesium, Cahn (1953 a) for orthorhombic uranium, and others. The best and most general treatment is by Laves (1952, 1954).

To examine the actual motion of the atoms the only possible course is to project the structure on to the plane of shear, to draw the trace of the plane of glide (K_1) in a suitable position (it has been customary to draw it to coincide with a row of atoms on the projection), then to put all atoms on one side of this trace through the requisite shear and to compare the atomic sites so attained with the final positions which they must have in the final state. This is of course known because the orientation of the second individual is known from the twin symmetry. In fig. 15 this has been done for a twin with $K_1=(130)$, $\eta_2=[110]$, in alpha-uranium, and it is seen that quite large adjustments or *shuffles* are necessary after the shear. The small arrows in the figure express the presumption that the shear and shuffles are not successive events but combine to force the atoms to move along non-parallel paths.

1.3.2.1. *Laves' Treatment.*—For any given atom N , Laves terms the shear path itself S_N (a vector), and the shuffle R_N . The magnitude and direction of both these vectors depends upon the position of the atom and on the precise location of the plane of glide (i.e. the interface). In the case illustrated in fig. 15, for instance, R_N points straight towards the interface for the atoms originally close to one side of it, but tends to become parallel to S_N for atoms further out. Quite generally, Laves points out, $\Sigma R_N \neq 0$ when the interface is drawn to coincide with a sheet of atoms. This resultant vector of all the shuffles will either point straight towards or straight away from the interface, according to the particular sheet of atoms of the structure through which the interface is made to pass. There is always a possible position for the interface, however (not coinciding with any atoms), for which $\Sigma R_N = 0$ and $\Sigma |R_N|$ is a minimum; this seems to be the best way to project the twinning process. Barrett (1948) suggested that the state of distortion at the interface depended on the exact position of the interface. This is correct, but as Laves points out, the growth of one individual at the expense of the other takes place by a gradual motion of the interface in a direction normal to itself, and it will therefore pass in rapid succession through dilatational and compressional stages.

Laves finds empirically that if t is the mean interatomic distance in the structure, then $Q = \Sigma |\mathbf{R}_N|/tN \sim 0.2$, for tin and magnesium; i.e. the arithmetical mean of the shuffle vectors is about one fifth of the mean interatomic distance. From published drawings for two mechanical twin laws in uranium (Cahn 1935 a), Q has been computed to be about 0.2 in each case. Since all hexagonal close packed metals have rather similar twinning mechanisms, it is probable that Q is roughly the same for all, but this has not yet been rigorously confirmed. There is some evidence, then, for Laves' suggestion that there may be an approximate critical

Fig. 15



Atom motions in a mechanical twin in uranium, projected on (0001).
(From Cahn 1953 a.)

value of Q , which, if exceeded, makes it unlikely that the twin in question will be capable of being formed.

Since a twinned lamella forms by a gradual sideways migration of one or both interfaces, the fact, usually stressed as being important, that atoms remote from the interface in a drawing such as fig. 15 appear to move almost parallel to the shear direction and to each other, is actually without any significance. Only atoms in the immediate vicinity of the instantaneous position of the interface are moving relative to each other, therefore only this part of the drawing is physically significant.

Laves' treatment is illuminating and easy to apply for simple structures such as tin, magnesium and uranium, but it is perhaps preferable to

keep to a qualitative account of the atomic movements when dealing with more complex structures. Thus, in the case of mechanical twinning in calcite, the calcium and carbon ions require no shuffles, but each group of oxygen ions has to rotate as a group. In estimating Q one would have to select arbitrarily one of several interatomic distances to serve as unit distance. However, a rough and ready way to meet this difficulty would be to use as unit distance for each kind of atom the mean of the distances of its nearest neighbours. The qualitative description here brings out the important point that the covalent C-O bonds are not disrupted but only rotated as a group. This rotation is probably easy to achieve. Thus Tahvonen (1947) has shown by diffraction methods that the NO_3^- groups, in the structurally very similar compound KNO_3 (rhombohedral form), are in a state of violent oscillation about the triad axis. The impossibility of breaking such powerful bonds by mechanical means without fracturing the whole specimen no doubt accounts for the impossibility of producing the other twin laws of calcite mechanically. The same consideration at once accounts for the lack of mechanical twinning in diamond and the related metals (but does not explain its absence in the face-centred cubic metals). See also the comments on the twinning of aragonite in § 1.3.1.6.

1.3.3. *Effect of Order on Mechanical Twinning*

Laves (*loc. cit.*) first pointed out that if his criterion of capacity for mechanical twinning ($Q \sim 0.2$) is valid, then the establishment of crystallographic order in a previously disordered alloy or compound might remove its ability to twin. Thus in iron, twinning mechanically with (112) as twin plane, no shuffles are needed because all atoms are at restorable lattice points, and $Q=0$. He shows, however, that if an alloy having the same structure, such as 50/50 brass, is ordered, the result of the shear would be to produce an orthorhombic (cf. fig. 16) structure with a unit cell of sides a , $a\sqrt{2}$ and $a\sqrt{3}$ —a martensitic phase transformation, in fact. Very large shuffles would be needed to restore this structure to an ordered body-centred one, so large that $Q=0.5$. Experimental proof of the prevention of twinning through the establishment of order in alloys is as yet lacking, but Laves has shown that the artificially prepared substance analbite, which is natural albite ($\text{NaAlSi}_3\text{O}_8$) in which the distribution of the Na and Al atoms has been made random by heat treatment, can readily be twinned by poking crystals with a needle. Albite, the ordered form, cannot be twinned, in spite of protracted attempts (Mügge and Heide 1931). (Buerger 1945, does claim to have twinned albite mechanically.) Similar conditions explain why dolomite, which is $\text{CaMg}(\text{CO}_3)_2$, and is ordered, cannot twin mechanically with (1012) as twin plane, though calcite, which is isostructural, twins very easily according to this law.

Experiments are currently in progress by the writer to test Laves' prediction with ordered iron-aluminium solid solutions containing about

25 atomic per cent of aluminium. The disordered form of these solutions is known to be capable of twinning.

1.3.4. *Twinning as a Function of Structure Type*

In the preceding sections we have established some generalizations about conditions necessary for twinning. Whether alone or in combination, these conditions do not seem to be sufficient ones. If a particular substance is found to twin according to a particular law, is there any assurance that other crystals isomorphous with it, or of closely similar structure, will also be found to do so? This, if true, would take us somewhat further in the search for necessary and sufficient conditions for twinning. Unfortunately, while isostructural sets of substances do often form twins, there are also many exceptions.

A good example of such a set is provided by the close-packed hexagonal metals. These depart from strict close packing by varying extents, having axial ratios in the range 1.59–1.89. Yet all readily form mechanical twins according to the same twin law, $K_1=(10\bar{1}2)$, $K_2=(\bar{1}012)$. The rhombohedral metals, antimony, bismuth and arsenic, similarly behave as a group.

Again, until recently iron and wolfram were the only body-centred cubic metals known to be capable of mechanical twinning. Now chromium (Carrington 1953) has been shown to do so, and so has molybdenum (Bechtold 1953, Cahn, unpublished work). Calcite and Chile saltpetre (NaNO_3) are isostructural and both capable of twinning mechanically.

Among growth twins there is not much evidence of this sort. One isostructural group which forms twins consists of aragonite, CaCO_3 , cerussite, PbCO_3 and strontianite, SrCO_3 , but another similar carbonate, witherite, BaCO_3 , is not reported as having twins. Among the plagioclase feldspars, which form a continuous isomorphous series from albite (Na , K) AlSiO_8 to anorthite, $\text{Ca}_2\text{Al}_2\text{SiO}_8$, twins are found at all compositions according to the same laws (cf. Donnay 1940). Donnay also cites evidence in support of the hypothesis that such twins are the thinner, the smaller the angle of obliquity.

The elements with the diamond type structure form growth twins very readily. Diamond has both contact and (commonly) penetration twins, with (111) as twin plane (Slawson 1950) while germanium (Ellis 1950, Ellis and Fageant 1954) and silicon (Salkovitz and von Batchelder 1952) form contact twins very readily according to the same law. Nothing is known about twins in grey tin. On the other hand, while copper, α -brass and face-centred iron readily form annealing twins, aluminium does so only rarely. In this particular case, the reason for the difference in behaviour has been discovered (cf. § 2.1.4).

A striking instance of the failure of isostructural substances to behave alike is provided by sodium chloride and galena. The latter twins profusely during growth, and by mechanical action, at high pressures and temperatures, according to a variety of laws. Sodium chloride will

not twin at all, except under very special conditions, and then only rarely. Here we must certainly take account of the difference in the type of bonding. In galena the atoms are connected by covalent bonds, while sodium chloride is purely ionic. C. P. Fenimore (private communication to J. D. H. Donnay) has pointed out that because of the purely ionic bonding in this substance, the numerous second-nearest neighbours play a greater part in determining the internal (electrostatic) energy of a crystal than the nearest neighbours. Since the second-nearest neighbour distances are altered at a twin interface in sodium chloride, this may be the reason for the sluggish twinning. In galena only the nearest neighbours, which alone are covalently bonded to the central atom, can appreciably affect the local energy of the interface, and the distances of these neighbours are unaffected by twinning. While covalent bonding may thus favour the occurrence of growth twins, the difficulty of breaking strong bonds by mechanical action excludes mechanical twinning in substances such as diamond and germanium in which the bonding is very strong. Galena has never been twinned artificially by mechanical means even under hydrostatic pressure, but the very careful goniometric work of Seifert (1928) leaves no doubt that many twins in natural galena were formed by shear, presumably when the material was in the earth under high hydrostatic pressure and at high *temperature*. Such conditions apparently permit the breaking of bonds in twinning without disintegration of the material.

We must conclude that the fact that two substances are isostructural is but a slender guide to a possible similarity in their twinning behaviour.

§ 2. GROWTH AND TRANSFORMATION TWINNING

2.1. *Experimental Facts*

Some of the experimental information on growth twins has already been referred to in § 1.3. It remains to fill some gaps and to discuss in more detail the twinning associated with phase transformations.

2.1.1. *Contact and Penetration Twins—Twin Interfaces*

The interface or composition surface between the individuals constituting a twin is something quite distinct from the twin plane, where there is one. The latter is a plane of structural symmetry between the components, while the interface may or may not be plane, and may or may not be parallel to the twin plane. When the interface is parallel to the twin plane, the edifice is termed a contact twin. The term has also been loosely applied to rotational twins such as those in zinc blende (§ 1.3.1.2) where the interface is a plane normal to a twin axis, or parallel to the axis, as in 'pericline' twins in albite. When the interface is crystallographically irregular, so that the components appear as if they had grown simultaneously but independently of each other, the edifice is called a penetration twin. Figure 2 is an example.

2.1.1.1. *The Rhombic Section.*—There is some justification in regarding twins possessing a twin axis as contact twins if they have a plane interface

parallel to the axis because such a plane has a special crystallographic significance, as was pointed out by Friedel (1926, p. 438). Figure 9 (b) represents a twin by pseudo-merohedry. Figure 9 (c) is a projection of the lattice of one individual of the twin along the twin axis AB, i.e. a projection into a geometrical plane P which almost, but not quite, coincides with a lattice plane P' that includes the row AD. For the present purpose fig. 9 (c) could be regarded as the projection of a *single* lattice plane P'. Let the lattice point X be in the plane of the paper; a line XY can be drawn through this such that all points to one side of it are projections of lattice points which are in fact above the paper, while those on the other side are projections of points below the paper. XY is identical with the line of intersection of P and P'—i.e. of the plane normal to the twin axis and of the lattice plane pseudonormal to it. Let the lattice row normal to the paper and passing through X be the twin axis. Then any point such as *a* is transferred by twinning to a position *a'* which is directly above or below another point in the figure, such as *b*. The difference in height between *a'* and *b* is the smaller, the closer *b* is to the line XY. This is because *a* and *a'* are both at the same height *H* above the paper, *b* is the same distance below the paper, and *H* is larger for points more remote from XY. Therefore the immediate neighbourhood of XY provides the optimum fit between the lattices of the two individuals. In three dimensions, the geometrical plane defined by XY and the twin axis through X is the surface of best fit. This plane, which is not parallel to any lattice plane, has been termed the *rhombic section* by Friedel.

Twins possessing a twin axis often have the rhombic section as interface and always so when the individuals are lamellar, just as those possessing a twin plane minimize interface distortion by having this plane as an interface. For a mechanical twin of the second kind, the rhombic section is identical with K_1 , the plane of glide, while the twin axis corresponds to η_1 . K_2 corresponds to the plane P' pseudonormal to η_1 , while XY is normal to the plane of shear. There is of course a similar correspondence between mechanical twins of the first kind and growth twins possessing a twin plane. The interface is thus the same irrespective of the origin of a twin so long as the interface in a mechanical twin is parallel to K_1 . This is always accurately so in non-metals, and approximately true in metals.

2.1.1.2. *Penetration Twins*.—No satisfactory interpretation of penetration twins exists. Such twins are quite widespread. Thus even diamond, which can form contact twins with an exceptionally smooth fit at the (111) interface (§ 1.3.1.1), mostly appears in the form of penetration twins, although the fit can hardly be better at any other surface than it is at (111). Probably the excellence of fit does not vary greatly with the orientation of the interface for highly symmetrical structures such as diamond, fluorspar or pyrite, but one would intuitively expect the variation to be greater for substances of lower symmetry. Inasfar as smooth fit at the interface determines ease of twinning, penetration twins

should be most common in highly symmetrical structures, and for pseudo-merohedral twin laws they should be more common when the obliquity is particularly small. No mineralogical classification for testing these predictions is known to the writer.

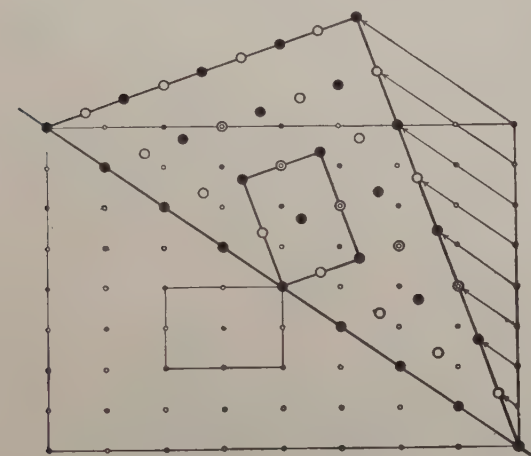
2.1.1.3. *Twins in Metals—Coherent and Non-Coherent Interfaces.*—Metallurgists use a terminology of their own. An interface parallel to a twin plane is called a *coherent* interface, while any other interface is termed *non-coherent*. Only one rotational twin law in a metal is known, so no terms have been introduced for this case.

Twins formed in cubic metals during recrystallization in the solid state (annealing twins, cf. § 2.1.4) assume one of the four shapes A, B, C, and D shown in fig. 17. XY is here the surface trace of the $(\bar{1}11)$ twin plane. Where an interface is neither parallel to $(\bar{1}11)$ nor congruent with an intergranular boundary, it is non-coherent; this is seen at C and D in fig. 17. Fullman (1951) in a series of elegant experiments established that in copper non-coherent interfaces are approximately parallel to $(\bar{1}31)$, (535) respectively in the two individuals. Both these planes belong to the zone of a $[101]$ direction which is common to both individuals. Whitwham *et al.* (1951) have shown that in aluminium a non-coherent interface has a stair-like appearance under high magnification, with treads parallel to (111) . It is surprising that in these metals interfaces parallel to (112) in each individual are never observed. The $(\bar{1}31), (533)$ interface, though having high indices, is apparently of lower energy.

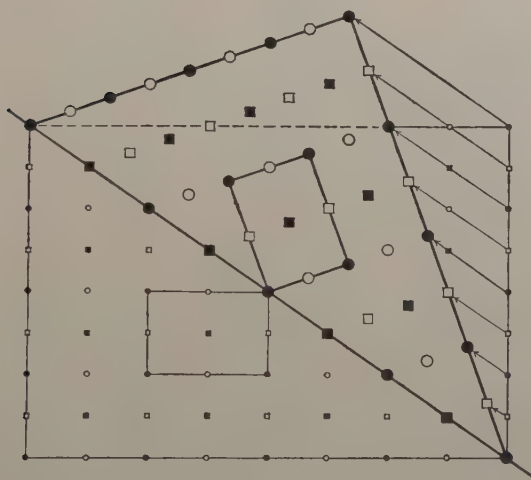
The twinned ingots obtained by freezing germanium or silicon (Ellis 1950, Ellis and Fageant 1954, Salkovitz and v. Batchelder 1952) have been found to originate from one nucleus, so that all the many individuals making up the ingot are related to their neighbours by twinning with (111) as twin and contact plane. Often two individuals B and C, related to an individual A by reflection in different (111) planes, impinge on each other, or else A may touch an individual D which is twin-related to B or C. A/D or B/C constitute *second-order twins*. This is the metallurgical equivalent of a repeated twin such as that in fig. 1. Second-order twins are also sometimes found in recrystallized copper (Whitwham *et al.* 1951). These authors applied the Friedel theory and showed that in cubic substances individuals constituting second- or third-order twins were in fact in twin relation. Thus for second-order twins the twin (symmetry) plane is (221) or (441) , and for third-order twins it is (552) or (511) , or else (721) . They found that while for these high-order twins the interface is never parallel to any of the twin planes, it is often plane and has rational indices. (But Ellis and Fageant 1954, report a well-defined interface between third-order twin-related crystals in germanium parallel to (532) in *each* crystal.) For second-order twins in copper, the interface is normally parallel to $(11\bar{1}), (15\bar{1})$ in the two individuals (Whitwham *et al.* 1951, Sharp and Dunn 1952). In both copper and germanium (Ellis and Treuting 1951) second-order twin interfaces were also found along

$(57\bar{5})/(13\bar{1})$ and $(\bar{1}41)/(10\bar{1})$. All six of these planes belong to the zone of $[101]$, which is a vector common to both individuals. This is the same relation as was found by Fullman for the $(\bar{1}31)/(\bar{5}35)$ non-coherent interface in *first-order* twins in copper. Although the quality of the fit at such

Fig. 16



(a)



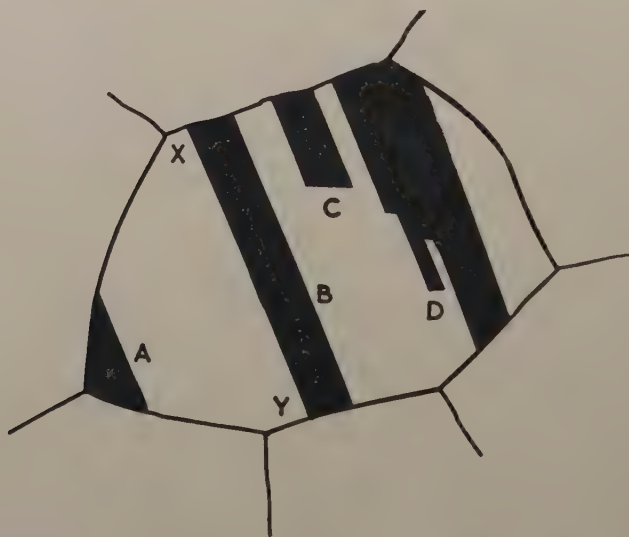
(b)

Atomic motions in the twinning of a 50/50 alloy with the body-centred cubic structure. $K_1=(112)$, $\eta_2=[11\bar{1}]$. (a) Black symbols represent atoms in plane of projection, open symbols those in adjacent planes. (a) Disordered alloy—all atoms equivalent; (b) ordered alloy—circles represent atoms of metal A, squares those of metal B. The structure is altered by the twinning shear. (Drawing furnished by F. Laves.)

interfaces has not been analysed in detail, the fact that they all include a lattice row common to both individuals suggests that the fit is good.

2.1.1.4. *The Energies of Twin Interfaces*.—Because of the good fit, one would expect the specific energy of twin interfaces to be particularly low in comparison with the specific energy of an interface between individuals in arbitrary mutual orientation (intergranular boundary). This is borne out by measurements of specific energy which have been made on annealing twins in polycrystalline metals, but not for mechanical twins (§ 3.1.8). In the case of annealing twins this was done by two techniques. One technique involves measurement of the equilibrium angle at which the interface between the two twin components meets the interfaces between these components and a neighbouring grain. In the other technique, the angle measured is the dihedral angle of the surface groove formed at high

Fig. 17



Configuration of annealing twins in face-centred cubic metal.

temperature where the twin interface meets the free surface of the specimen. In each case the specific energy of the two reference interfaces is known from other experiments. Details of these methods are reviewed by Burke and Turnbull (1953).

For annealing twins in copper, the ratio between the specific energy of a coherent (111) twin interface and that of a random intergranular boundary is 0.03–0.05 (Fullman 1951). For annealing twins in aluminium, however, the corresponding ratio is 0.21, in spite of the structural identity of the two metals (Fullman 1950 b). An explanation of the difference must no doubt be looked for in terms of differences in the law of interatomic force in the two metals. (The difference again emphasizes the point that structural identity is a poor

guide to twinning behaviour.) The ratio of specific energies for a non-coherent interface parallel to $(131)/(535)$ of the two individuals (Fullman 1951) is about 0.80. Dunn, Daniels and Bolton (1950) have similarly studied the energy of coherent and non-coherent twin interfaces in body-centred iron containing 3.5% of silicon (added to eliminate the polymorphic transformation). The ratio is about 0.22 for the coherent interface and again about 0.8 for a non-coherent interface. The twins were obtained by recrystallization from seeds of controlled orientations, since spontaneous annealing twins are rarely found in iron. The interface was initially non-coherent, but spontaneously became parallel to (112) during continued annealing.

No energy measurements have been made for twin interfaces in metals with the diamond structure, but there are structural reasons for believing that this energy is exceptionally small (cf. § 1.3.1.1). Experimental energies would be difficult to get in these metals since they cannot be recrystallized, and are probably not liable to surface evaporation.

Thermal and chemical etching has little effect on a coherent twin interface in silver (Chalmers, King and Shuttleworth 1948), iron (Dunn, Daniels and Bolton 1950) and in aluminium (Lacombe and Yannaquis 1947), though intergranular boundaries are vigorously attacked. This is a reflection of the lack of structural distortion at the coherent interfaces. Non-coherent twin interfaces are attacked.

2.1.1.5. *Melting-point of Twin Interfaces.*—There is reliable evidence that intergranular boundaries in polycrystalline metals melt at a temperature a fraction of a degree c lower than the bulk material. Chaudron *et al.* (1948) showed this for pure aluminium, as did Pumphrey and Lyons (1949). From an illustration in Chaudron's paper it can be deduced (Chalmers 1949) that the melting-point depression is about 0.25°C for an ordinary intergranular boundary; Pumphrey and Lyons give a figure of roughly 4°C . Chaudron *et al.* state that *coherent* twin interfaces do not have a lowered melting-point, although *non-coherent* ones do. From the available evidence it is not certain whether the lowering of melting-point is genuine or caused by adsorbed impurities. If impurities are responsible, evidently they are not adsorbed at the low-energy twin interfaces.

Chalmers (1940) determined a melting-point depression of 0.14°C at intergranular boundaries in tin, but noted that the interfaces of mechanical twins (approx. parallel to the twin plane) do not share this depression.

2.1.1.6. *Diffusion at Twin Interfaces.*—There is some evidence that self-diffusion at a mechanical twin interface in tin is slower than at an ordinary intergranular boundary (Fensham 1950). At a twin interface indeed diffusion appears to be no faster than the 'volume' diffusion inside a grain. This, and Chalmers' observation of the previous paragraph, show that the interface in tin is in a low state of strain, unlike interfaces of some other mechanical twins (§ 3.1.8).

Barnes (1950) found that the diffusion of copper in nickel is no faster at a coherent annealing twin interface than it is inside a grain, though at ordinary intergranular boundaries diffusion is faster.

2.1.2. *Cohesion at Twin Interfaces*

Contact twins originating during the growth of a specimen cohere so firmly that fracture generally occurs within one of the individuals, on a cleavage plane if there is one. When the interface is not 'coherent', however (i.e., when it is parallel neither to a symmetry plane nor to a rhombic section), the twin often breaks preferentially at the interface. The cohesion is often quite weak. This is not the case for true penetration twins like that illustrated in fig. 2, and this reinforces the view that in such twins the interface is still one of comparatively good fit. However, there are certain intermediate cases (Friedel 1926, p. 441) where the two individuals are in contact along only a single 'non-coherent' interface, determined merely by the different rates of growth in different directions. Such twins, which are found for instance in gypsum and rutile, fracture easily along the interface.

Intergrowths which by chance are nearly but not quite in twin relation are but weakly coherent and easily separate along the interfaces (e.g. Johnsen 1907). This suggests that the low specific energy and consequent high cohesion of a coherent interface is vitiated by even small departures from the correct orientation relationship, a supposition which has had some direct experimental confirmation (Dunn, Daniels and Bolton 1950).

Many metals behave differently from minerals in that random intergrowths cohere just as strongly as do single crystals. Under abnormal conditions, however, such as stress corrosion, ordinary intergranular boundaries are attacked and then fail under applied stress, while twin boundaries do not. This applies to annealing twins, but not to mechanical twins, which may be sources of exceptional weakness. The evidence about this is reviewed in § 3.1.9.

2.1.3. *Influence of Conditions During Crystallization*

2.1.3.1. *Supersaturation*.—When crystals capable of twinning separate from a solution or magma, supersaturation favours the deposition of twins as opposed to single crystals (Johnsen 1907, Buerger 1945, Deicha 1949). If a constituent added to a solution increases its viscosity greatly, the solution can more easily be made supersaturated and then a high proportion of twins will eventually deposit. There is some rather uncertain evidence that artificially induced viscosity even in the absence of pronounced supersaturation favours twinning. In an elegant experiment Johnsen (1907) ground finely some coarsely twinned magnesium sulphate; the fragments were then predominantly single crystals. This powder was placed in a saturated solution of the salt, which was then diluted, but not sufficiently to allow all the added solid to dissolve. Under these conditions there could be no supersaturation. When the solution was cooled, almost all the crystals which grew large were single.

(A solution of lithium sulphate behaved similarly.) Another lot of solution was made viscous by adding borax, and could then be made supersaturated by cooling. All the crystals which eventually separated spontaneously were twinned. These crystals were again finely ground and added to some more supersaturated solution containing borax. In spite of the predominance of single crystalline fragments in the powder, this time only twins were deposited from the solution. This experiment clearly illustrated the influence of supersaturation. The part played by the viscosity in itself is uncertain. Thus the facilitation of twinning in crystals of barium chloride separating from solution made highly viscous with rubber latex, reported by Lehmann (1877, 1884) was not confirmed by Mügge (1888). However, Mügge himself later (1911) thought that the available evidence pointed to an intrinsic evidence of viscosity.

Related to these observations is the fact that twinned nuclei, *once established*, grow faster than do single crystal nuclei. This has been verified by direct observation by Scacchi (referred to by Johnsen 1907). This is not in contradiction with Johnsen's observation that a barely saturated solution selects untwinned nuclei for further growth, for, as Johnsen points out, *small* twins, which have a comparatively high surface volume ratio (because of re-entrant facets), will preferentially redissolve in the course of the small fluctuations in temperature which always occur in a cooling solution, if the supersaturation is so slight that these fluctuations may momentarily remove it.

Deicha (1946, 1948, 1949) dissolving sodium chloride in distilled water and, taking care to avoid premature nucleation, was able to supersaturate the solution and thus caused it to deposit twinned crystals. The twins were not the expected kind with (111) as twin plane; the twin plane appeared to be (332). The crystallography of these twins needs clarifying. Deicha also remarks that twinning in deposited gypsum crystals is encouraged by the supersaturation, and that sulphur crystals freezing from a supercooled melt are frequently twinned. In his 1949 paper he showed that supersaturation was necessary for twinned crystals of barium chloride to be obtained from solution.

Lithium sulphate is normally twinned only in the presence of impurities (cf. next section), but controlled high supersaturation yields twinned crystals even from pure solution (Rae and Robinson 1954).

2.1.3.2. Influence of Specific Impurities.—Substances which do not by themselves readily form twins can sometimes be made to do so by adding specific impurities. This may perhaps be regarded as a specific form of the many instances of drastic modification of crystal habit wrought by traces of impurity (cf. for instance the review by Buckley 1951, p. 339), though quite large amounts of additive may be required to produce twins. Scacchi (quoted by Johnsen 1907) found that lithium sulphate deposited from solution was twinned if the solution contained potassium sulphate; sufficient potassium was included in the twinned

crystals to be faintly detectable by means of a spectroscope. Löffler (1934) in an elegant series of experiments on the crystallization of sodium chloride and potassium chloride, showed that a number of metallic chlorides, themselves present to the point of saturation, could produce perfectly formed penetration twins of both salts, with (111) as twinning plane. The added chlorides (in particular MnCl_2) substantially increase the viscosity; this, however, is not the important factor, for other agents producing viscosity, such as gelatine, were ineffective. The 'effective' chlorides all had cations with radii sufficiently close to those of sodium (or potassium) to permit isomorphy. The added cation was not present in the deposited crystals in a sufficient concentration to permit detection, however.

The power and specific nature of such additions in producing twinning is illustrated by the fact that if sizeable untwinned crystals of lithium sulphate are brought into a saturated solution of lithium sulphate also containing potassium sulphate, numerous crystallites become attached in twin position, but only on one particular family of crystal face (Johnsen 1907). In one instance, the function of the additive has been elucidated. Von Glazczynski (1948) found twins (he does not consider them 'genuine twins') in pseudobrookite which are caused by the epitaxial deposition of anatase, TiO_2 , during growth. Such deposition is usually followed by further accretion of pseudobrookite in twinned orientation. The particular twin laws elicited in this way are not found in the absence of anatase.

2.1.3.3. Single or Repeated Nucleation.—The normal way for a penetration twin to form, to judge by the appearance of the finished product, is for a minute twinned nucleus to appear spontaneously, followed by the growth at roughly equal rates of the two individuals. Contact twins probably also form in this way when both individuals are of roughly the same size and shape, as often happens, but if the individuals are lamellar in form, or even polysynthetic (consisting of very many fine lamellae), some other mechanism has to be postulated. Mügge has supposed that all such twins are mechanical in origin, even though many of these twin laws cannot be produced by artificial mechanical means. There is some indirect evidence in favour of this view in the form of successful attempts to make mechanical twins in normally recalcitrant crystals by applying high temperature and pressure, conditions to which nascent minerals are often exposed (cf. § 3.1.2). On the other hand, lamellar twins are frequently made in the laboratory by separation from supersaturated solutions (e.g., the barium chloride twins made by Deicha 1949). It is true that this substance can twin mechanically also, but it is hard to see why mechanical twins of appreciable size should be formed under such peaceful conditions of crystallization. Laves (1952) has suggested that the much debated polysynthetic twin lamellae in the plagioclase feldspars were formed mechanically when the crystals were hot enough to be disordered, for disorder here makes possible twinning under stress, which

is not found at lower temperatures (cf. § 1.3.3). He offers some positive evidence of an optical nature in favour of his interpretation. This question is raised again in § 2.2.2.

It is however highly probable that where the twin law is of the reflection type, lamellar twinning is mostly caused by the generation of *stacking faults* during growth. By this term is meant the addition of a monomolecular plane nucleus in twin orientation parallel to the twinning plane which then covers the face. Further layers are added in twinned orientation until there is another stacking fault restoring the original orientation. Experiments have made it virtually certain that this is just how annealing twin in face-centred cubic metals grow (§ 2.1.4). A good test for the correctness of this theory for minerals and artificial compounds would be to survey the morphology of those substances having lamellar twins, for it is requisite that the twin plane should always also be an observed crystal face, at least in the early stages of growth. Hartman (1953) has put forward a detailed structural theory to account for the variety of observed morphology, and concludes that twins would be expected to form on the slowest growing faces (which are the ones that persist), apparently because several of the strongest chemical bonds are parallel to these faces and there is minimum opposition to an accidental stacking fault in consequence. For full details of Hartman's interesting views his dissertation must be consulted.

Donnay (1940) has collected information showing that the thickness of the fine polysynthetic twin lamellae in the plagioclase feldspars, which form a series of continuously varying composition, varies directly as the twin obliquity, and he interprets this very plausibly on the argument that if there is a small obliquity (i.e., a pronounced pseudo-symmetry), the difference between a correctly deposited monolayer and a stacking fault is especially small, and stacking faults are therefore frequent and twin lamellae thin. If the plagioclase lamellae are indeed mechanical in origin the true explanation must be a different one.

There is positive evidence that twins can be formed in certain minerals by the deposition of material in twin orientation on previously untwinned crystals of visible size, or even by the mutual adhesion, in twin orientation, of two fully formed crystals. One such piece of evidence, referring to lithium sulphate, was quoted in the last paragraph of the preceding section. Again, Goldschmidt and Müller (1934) found among more than 2000 augite twins many consisting of one large and one tiny individual, which points to such a mode of origin. Cerussite twins provided similar evidence (Goldschmidt 1902). Evidence for orientated adhesion was also obtained by Gaubert (1896) and impressively by Shaskolsky and Shubnikov (1933) who found that when a large number of small octahedra of alum were sprinkled on to a horizontal face of a large octahedron immersed in saturated solution, many adhered to the face, either in parallel or else in twinned orientations. It would seem that the interatomic forces here actually sufficed to move the crystallites into the

correct azimuth or at least instantly to retain them there as they moved about, with the solution acting as a form of 'glue'. Small *cubic* crystals of alum also adhered, in a position such that [110] rows of the large and the small crystals were parallel. This is one of the few examples of what Friedel (1933) calls *monoperiodic twins*. The other prominent example is the 'Zinnwald' twin law in quartz (Drugman 1928), in which the close-packed directions in both individuals are parallel. Neither this, nor the alum twins just mentioned, fit into Friedel's scheme of twinning. This scheme involves three dimensional coincidence lattices, hence normal twins are to be termed *triperiodic*.

2.1.3.4. *Metallic Twins formed during Freezing*.—Experiments on the growth of certain metallic twins suggest that the stacking fault mechanism operates exclusively in these cases. If germanium or silicon is slowly frozen in a crucible, a single crystal nucleates at one end and the whole copiously twinned ingot consists of successive orders of twinning related to the one starting orientation. The individual crystals are all in the form of lamellae, usually thick, in contact along the (111) twin plane. In the isostructural diamond, (111) is known to be the predominating growth face, so that the same may be presumed of silicon and germanium. Germanium can be grown virtually free of twins if a container is avoided altogether, by Czochralski's method of drawing a single crystal filament slowly out of a melt (Teal *et al.*, 1952). It is likely that mechanical pressure predisposes a growing face to harbour stacking faults—a kind of mechanical twinning on an atomic scale. Also it is known that deformation produces numerous stacking faults in a solid solution of silicon in copper (Barrett 1950) and in other metals and alloys; and germanium and silicon, which are known to be capable of being plastically deformed when hot (Gallagher 1952), may fault during constrained growth.

Twinning rarely occurs in castings of other metals (other than large mechanical twins occasioned by cooling stresses, as in zinc). Under the specific conditions obtaining in semi-continuous casting (extremely rapid cooling at the mould face followed by slower cooling further in) numerous coherent twin interfaces, parallel to (111) and roughly normal to the mould face, are found in pure aluminium. Presumably the very high rate of cooling engenders stresses which force stacking faults to form, though normally this metal is not predisposed to form such faults (see § 2.1.4: Hérenghuel 1948, Hérenghuel and Lacombe 1949). Aust *et al.* (1952) noted in addition that small amounts of impurity prevented the formation of twins. Oliver (1951) and Clark and Craig (1953) have published photographs of isolated growth twins in zinc and silver. These are distinctly unusual.

2.1.3.5. *Twins deposited from the Vapour Phase*.—The oriented condensation of metallic vapours on monocrystalline substrate such as alkali halides and mica has been much studied by means of electron diffraction. It has repeatedly been found that the deposits form a system

of polysynthetically twinned crystals. This seems to happen especially when the quality of fit between the lattices of the metal and the substrate is only marginal, so that the twinning is here a mode of accommodating strain (Kirchner and Cramer 1938, Menzer 1938, Elleman and Wilman 1948, 1949).

2.1.3.6. *Twins in Electrolytic Deposits*.—Polysynthetically twinned electro-deposits of copper have been recorded, all the lamellae being parallel to the same set of (111) planes (J. B. Hess, quoted in Barrett 1952, p. 516). Since electro-deposits are known to be in a highly stressed condition, this observation supports the contention that stress may promote stacking faults.

2.1.4. *Annealing Twins in Metals*

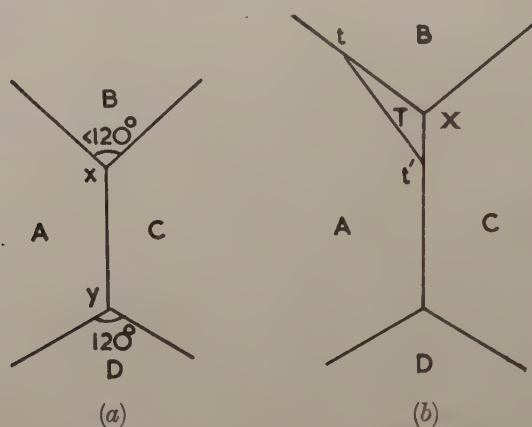
Recent research on this subject, which has been largely successful in accounting for the origin of the twins, has been ably reviewed by Burke and Turnbull (1953). This account will therefore be kept brief. (See also § 2.1.1.3.)

Annealing twins, as illustrated in fig. 17, occur only in certain face-centred metals, especially copper, brass, the face-centred cubic form of iron, silver, etc. Under very special circumstances they can be made in body-centred iron (Dunn *et al.* 1950). There are virtually no twins in cast ingots of these metals. The twins are progressively formed if the metal is deformed and then recrystallized. The important process is the passage of intergranular boundaries through the metal in the course of annealing—hence the name given to the twins. Harker and Parker (1945) and Smith (1948) have convincingly shown that, once a set of new grains is formed, any further boundary migration is due to lack of equilibrium at the edges where three boundaries meet. Normally equilibrium requires that the boundaries be inclined at 120° to each other, while this in turn is not consistent with the existence of an array of roughly equiaxed grains. The 'triple edges' where boundaries meet thus migrate through the material in a vain attempt to attain equilibrium, vain because as one triple edge approaches equilibrium another departs from it.

In fig. 18, let A, B, C, D be four grains meeting at two triple edges (points in the sectional view), X and Y. If the angle marked at X is smaller than 120° , the point X will move into grain B; this is equivalent to saying that grains A and C grow at the expense of grain B. During the growth of, say, grain A, a stacking fault may at any time occur, so that a twin is nucleated. Unless certain energetic conditions obtain, however, the twin will be unstable and another stacking fault will quickly restore the initial orientation. If these conditions are met, the twinned orientation will persist. It is required that the sum of the total energies of the three boundaries of the twinned individual T be smaller than the total energy which the boundaries Xt and Xt' would have if the region T had retained the untwinned orientation A. This is possible because (a) the energies of ordinary intergranular boundaries depend somewhat on the

relative orientation of the grains they separate, and (b) the energy of a coherent twin boundary such as tt' is very small (§ 2.1.1.4). Thus twins form progressively as boundary migration proceeds. Observation of specimens at successive stages of annealing, and measurements of grain boundary energies at locations where twins had formed, have provided evidence in support of the above interpretation (Fullman 1950 a, Fisher and Fullman 1951). Experiments by Burgers, Meijs and Tiedema (1953) on the influence of the orientation of a large crystal growing into a sharp texture of small grains on the frequency of annealing twins in it show clearly the importance of boundary energies in determining the survival of a twin. Burke (1950) has also done important experiments which led him to this conclusion. It seems that the isolated stacking faults produced by deformation, especially in brass, play a part in generating twins in the

Fig. 18



Genesis of an annealing twin. (a) Before annealing; (b) after annealing. The dashed line in (b) indicates the initial position of the A/B boundary.

early stages of recrystallization (before the deformed material is entirely consumed), as was shown by Maddin, Mathewson and Hibbard (1949), but other experiments show that this is certainly not the whole story (Mathewson and Horn 1930).

Annealing twins are rarely found in aluminium even after prolonged grain growth, but occasionally well-formed coherent twin interfaces are found (Dalitz and Burgers 1949, Fullman 1950 b). The paucity of these twins, as Fullman pointed out, must be due to the comparatively high energy of coherent twin interfaces in this metal (§ 2.1.1.4). As a result, the energy inequality referred to in the preceding paragraph will be satisfied only in rare instances; specifically, when T, B, and C have almost the same orientation, so that the T/B and T/C boundaries have low energy. This in turn implies that A should be *roughly* in twin orientation to B and C. In agreement with this, Burgers, Meijs and Tiedema (1953) showed that indeed crystals roughly in twin relation to the sharp texture into which they were growing were richest in twins.

Burgers (1946) discovered the strange phenomenon of *stimulated twinning* in aluminium. An advancing grain sometimes releases a submicroscopic fragment of crystal which happens to be in accurate (111) twin relationship to it and allows it to grow. The detailed mechanism remains in doubt. On the other hand, if a large growing crystal consuming a fine-grained matrix meets small grains approximately in twin relation to itself, it cannot consume these and they remain as island grains (Lacombe and Berghezan 1949, Tiedema, May and Burgers 1949). Such grains are probably bounded by a zigzag boundary consisting of low-energy coherent (111) and non-coherent interfaces, and these are stable. Indeed it is an accepted fact that whatever other boundaries may be able to migrate, a coherent (111) interface can never do so (e.g., Burke 1950).

2.1.5. Phase Transformations and Associated Twinning

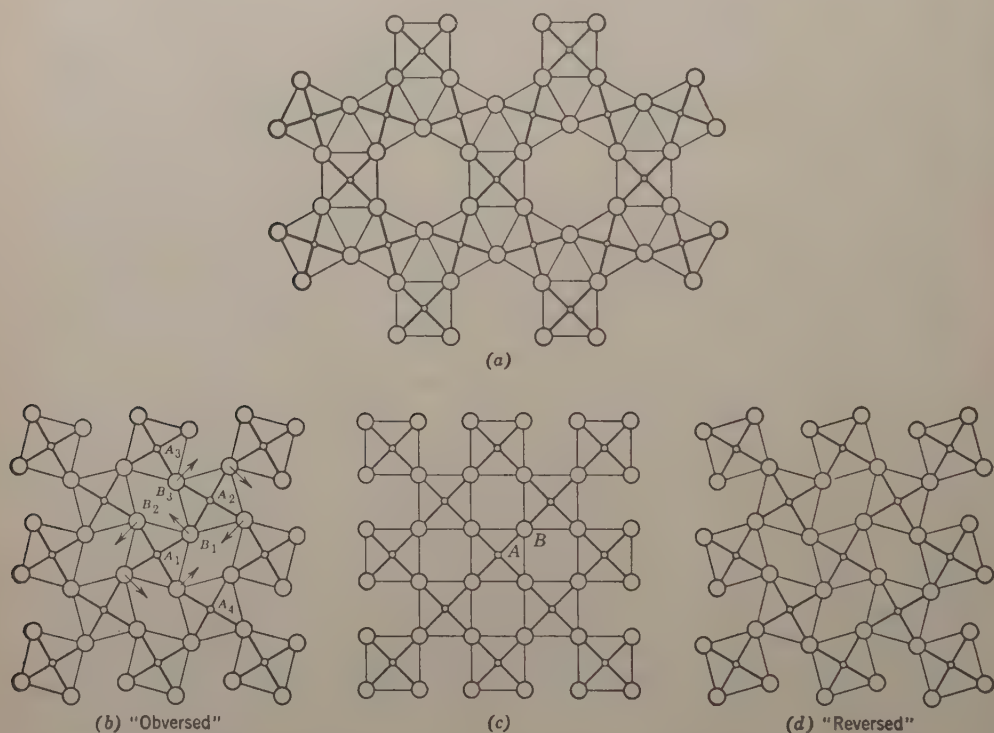
2.1.5.1. *Displacive and Reconstructive Transformations*.—Buerger (1951) in his illuminating review of the crystallographic principles of solid-state phase transformations, explains that the great majority of such transformations can be subdivided into *displacive* and *reconstructive*. In each case the nature of the chemical bonding is left unaltered, but the distribution and length of bonds is altered. In a displacive transformation, all atoms which were nearest neighbours remain neighbours, so that no bonds are broken. In a reconstructive transformation some or all of the bonds are broken and atomic neighbours are reshuffled completely; even the number of nearest neighbours may change. Transformations such as those from white to grey tin, where metallic is replaced by covalent bonding, fall into a separate category.

Figure 19, taken from Buerger's article, shows diagrammatically the two types of transformation. (c) is a highly symmetrical structure of four-coordinated ionic groups which can either disintegrate and be reconstructed as an (a), or else transform displacively into (b) or (d). The symmetry is reduced by the displacive transformation, and this is the reason why two alternative orientations are produced; the structure can collapse in either of the two ways. Only one diagram is necessary for the reconstructive transformation because normally the rupture of bonds prevents any orientation relationship between initial and final orientation. Nevertheless this is not universally true:—thus in the aragonite–calcite transition, which is entirely reconstructive (here even nearest neighbour distances are affected), there is a simple orientation relationship between the two phases.

In a displacive transformation from higher to lower symmetry, the distances and coordination symmetry of second nearest neighbours are altered. Some of the neighbours become closer than before which, as Buerger points out, leads to a reduction of free energy, so long as the bonds have wholly or partly ionic character. Hence the less symmetrical form has the lower free energy, and is stable, at low temperatures. At

high temperatures thermal oscillations locally simulate the symmetrical form, which becomes energetically preferred because most local configurations at any instant will approximate to the symmetrical structure so that the latter has a high entropy. It is indeed a universal rule in transformations that the form or forms stable at high temperature are more symmetrical than those stable at lower temperature.

Fig. 19



Preparatory twinning associated with a phase transformation. (a) Reconstructive transformation; (b), (d) displacive transformation; (c) is original structure. (From Buerger 1945.)

2.1.5.2. *Twinning as a Prelude to Displacive Transformations—Preparatory Twinning.*—Suppose we have a crystal of the low-temperature form of fig. 19, say in obverse orientation. If this crystal should become twinned with respect to a plane normal to the paper and parallel to A_2A_4 , the second individual would have the reverse orientation. The interface layer, in compromising between the two orientations, would assume the configuration characteristic of the high-temperature form (c). The greater the number of twinned individuals, the greater is the number of interfaces and the larger the fraction of the crystal which has effectively transformed to the high-temperature form. In this connection it should

be recalled that Aminoff and Broomé and others (§ 1.3.1) showed that the transition layer in a number of twin species adopted the structure of other polymorphic forms of the substance concerned.

The process just described is one of common observation in substances subject to displacive transformations. When a crystal of the low temperature form is heated, numerous thin twinned lamellae are formed *by shear*. As the transformation temperature (which may not be sharply defined) approaches, the structure generally approaches more and more closely to the higher symmetry which it will eventually adopt. In terms of fig. 19, this means that the small ionic groups in the obverse and reverse forms become more nearly parallel, and therefore the twin obliquity (and correspondingly the magnitude of the twinning shear) is reduced. This apparently diminishes the resistance to the formation of further lamellae, for they rapidly become more numerous and also much thinner, being often but a small fraction of a micron in thickness. In some cases the *preparatory twinning*, as we may term it, begins only a few degrees below the transformation temperature (e.g., nickel sodium uranyl acetate, Johnsen 1907), or else it may be spread over a wide range of temperature (aragonite). It also occurs in the course of the reverse transformation. The twinning may become so finely distributed that it becomes impossible to say precisely at what temperature the material has become a homogeneous crystal of the symmetrical form.

Many substances behaving in this way are listed and described by Friedel (1926, pp. 490, 574). They include leadhillite (sulphocarbonate of lead), calcium chloroaluminate, ammonium sulphate, potassium sulphate, several triple uranyl acetates, and a number of other salts.

The immediate cause of the twinning appears to be a thermally induced mechanical stress. In most of the substances concerned the approach to higher symmetry is accompanied by a change of axial ratios. Thus in aragonite the angle (110)–(110) alters from $63^{\circ} 48'$ at room temperature to virtually 60° at about 400°C , because of the increasing pseudo-trigonal symmetry. The coefficients of thermal expansion are therefore anisotropic and this is known to lead to severe mechanical constraints on heating polycrystalline aggregates (Boas and Honeycombe 1946). Even in single crystals lack of uniformity of temperature would have a similar effect. Thus Mügge (1888) observed that preparatory twinning was brought about in barium chloride crystals by placing the crystal on a cool metal plate with one end projecting, and heating this end in a flame. Touching a crystal face with a red-hot platinum wire called forth localized twinning, most of which disappeared when the wire was taken away. Such reversibility is lost when large volumes have been twinned.

At least one crystal transforming by a *reconstructive* process, aragonite, is subject to preparatory twinning, and eventually transforms via the polysynthetic twinned stage to an oriented calcite crystal. Aragonite would fit into Buerger's scheme of fig. 19 if, instead of drawing atoms, he had drawn lattice points. This is because aragonite twins according to

reticular pseudo-merohedry (§ 1.2.1.4). One half of the lattice points (and therefore a fraction of the atoms) shift into the positions appropriate for the twinned orientations by means of *small* motions, while in the case of true displacive transformations all the lattice points, and indeed all the atoms, behave in this way. Probably the mineral leadhillite, which behaves just like aragonite, twins by reticular pseudo-merohedry and transforms reconstructively, and perhaps some others. However, the large motions, necessary for the majority of the atoms in the shear twinning of these minerals is reflected by the fact that mechanical twins have never been obtained by stressing alone—a high temperature is absolutely necessary—and correspondingly the phase transformation is very sluggish (cf. also § 1.3.1.6 and § 2.1.5.4).

At least one case is known where the high temperature form is twinned and the low temperature form is not, in the strict sense. When a crystal of the hexagonal form of zinc sulphide (wurtzite) is heated, it transforms sluggishly into a crystal of the cubic form (zinc blende or sphalerite), at temperatures roughly in the range 900–1000°C. The cubic crystal is twinned with respect to a [111] twinning axis (cf. § 1.3.1.2). The hexagonal form normally contains increasing numbers of stacking faults on (111) planes as it is heated, producing streaks in x-ray patterns (Jagodzinski 1949). These faults are in effect preparatory twins of monoatomic thickness. Recently Piper and Roth (1953) made exceptionally perfect crystals of wurtzite by sublimation. These crystals contained no free dislocations (hence were unusually strong) and no stacking faults until a high temperature was reached; the two properties are doubtless connected. These crystals do not entirely transform to the cubic phase. Note that in this compound the stacking faults in the hexagonal form constitute layers of the cubic form, while the twin interfaces in the cubic form possess an atomic arrangement characteristic of the hexagonal form. In a sense, therefore, the transformation is never quite complete even with normally imperfect crystals.

Another substance which behaves very similarly to zinc sulphide is cobalt (Edwards and Lipson 1943). Cobalt is hexagonal close-packed at room temperature. On heating it acquires a large density of stacking faults (monolayers of face-centred cubic form) and eventually becomes entirely cubic. Presumably the high-temperature form is copiously twinned, although this point has not been examined.

2.1.5.3. Ferroelectric Crystals.—Ferroelectric compounds always crystallize in at least two modifications; the ferroelectric form, stable at low temperatures, deviates but slightly from the symmetry of the more highly symmetrical form. These compounds are therefore subject to transformation (preparatory) twinning. Instances are Rochelle salt (Ubbelohde and Woodward 1945, Klassen-Nekludova *et al.*, 1948); potassium dihydrogen phosphate (Ubbelohde and Woodward 1947); barium titanate (Kay 1948, Rhodes 1951); tungsten trioxide (Kirakawa

1952, Rhodes 1952). In these substances, the twinned lamellae are identical with the ferroelectric domains. The application of an electric field alters the thickness of existing twinned lamellae, as do direct mechanical pressure and simple heating (Kay 1948, Mitsui and Furuichi 1953). If the crystal has not previously been mechanically distorted and so does not have a curved lattice, it is indeed possible to remove all vestiges of twinning from a crystal of barium titanate by applying an intense field while the crystal is held above the transformation temperature, and cooling it through this temperature without removing the field. The mechanical action exerted by the field eliminates all portions in reverse orientation and leaves only the obverse (Wood 1951). Thus barium titanate, and probably the other compounds referred to, can be twinned or untwinned indifferently by mechanical, thermal and electrical means.

The twinning patterns in barium titanate, particularly in thin specimens, can be highly complex. Such patterns apparently minimize the elastic strain energy (Matthias and von Hippel 1948, Forsbergh 1949, Merz 1949). These references are but a selection from a growing body of published work.

The transformations of the type discussed in this and the preceding section are difficult to classify thermodynamically, because one form merges virtually continuously into the other. This difficulty is discussed by Tisza (1951) and Matthias (1951).

2.1.5.4. Hybrid Crystals.—A number of transformations are known in which a single crystal of the low temperature form yields an assemblage of crystals of the high temperature form which either have closely similar orientation, with a spread of perhaps a few degrees, or else all have one axis approximately parallel but random azimuth about this axis. Such an assemblage has been described by the term *hybrid crystal* (Ubbelohde and Woodward 1945). In some such cases twinning probably plays no part in the transformation (e.g. the lower phase transformation in uranium, Cahn 1953 b), but in other cases, thermal twinning has been detected. Thus Kennedy, Woodward and Ubbelohde (1953) studied the transformation in potassium nitrate, which is closely similar to the aragonite-calcite transformation (cf. § 2.1.5.2). So long as the crystal was not dehydrated, the result of transforming a single crystal into the trigonal form and back again was to give a hybrid crystal with the pseudo-trigonal *b* axis roughly parallel throughout. The component subunits were themselves finely twinned. The authors suggest that the subunits are the result of the growth of imperfectly orientated nuclei. The stresses occasioned by the impingement of separate subunits during growth must give rise to profuse twinning.

2.1.5.5. Martensitic Transformations.—This name is applied to transformations involving the cooperative motion of large numbers of atoms in a manner closely related to shear twinning. It is found that the product of such a transformation may be intimately twinned, and it has

been suggested that twinning plays an essential part in the cooperative motions referred to (Bowles and Mackenzie 1954). In one case the origin of the twin lamellae in the low temperature form has been interpreted in detail (Basinski and Christian 1954 b). This type of transformation is further discussed in § 3.2.7.

2.1.5.6. *Memory Effects in Quartz*.—The α - β transformation in quartz is associated with a number of abnormal features, one of which is a memory effect. A trigonal, optically active low temperature form of quartz transforms displacively to an optically neutral hexagonal form at 573°C. The low temperature form can be optically of either sign (usually the crystal is entirely of one sign, though ‘optical twinning’ does occur); also it may be twinned according to the Dauphiné law (180° rotation about a twin axis parallel to the triad axis), with an irregularly shaped interface.

It is found that if a trigonal, untwinned crystal is heated above 573°C and allowed to cool again, it will almost invariably have the same single orientation as before (Fron del 1945, Armstrong 1946) while a twinned crystal would correspondingly be twinned again on cooling. Zinserling (1941, 1953) showed that certain varieties of quartz, if taken into the hexagonal form and cooled again, exhibit the same *pattern* of twin individuals as before; i.e. the interfaces had the same shapes. This was also confirmed by Armstrong (1946). Quartz which behaved like this was generally ‘smoky’, and capable of being coloured by x-rays. This is generally regarded as a sign of impurity content, and Zinserling postulates that the impurities are concentrated at the interfaces. The suggestion is that the impurities remain where they are even above 573°C and form barriers to the growth of twin individuals as the crystal cools. It is not explained why twins form at all on cooling, and the same number of them as initially.

Certain peculiarities in the shape of the interfaces in quartz crystals containing both Dauphiné and optical twinning which have been reported (Pérez 1952), point to an attempt by the twinned crystal to increase the area of some interfaces at the expense of others, as in the genesis of annealing twins (§ 2.1.4).

2.2. *Theory*

Many theoretical ideas relating to growth and transformation twinning have been incorporated in the preceding sections, to avoid splitting up the subject matter excessively. Here we shall briefly review some ideas which could not conveniently be introduced earlier.

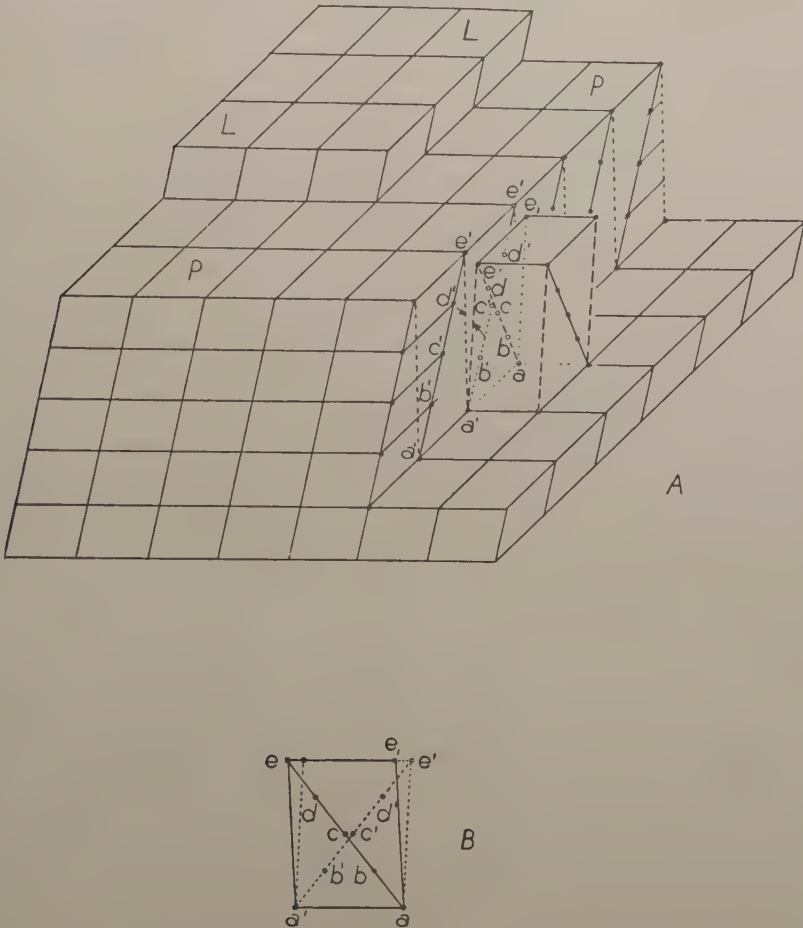
2.2.1. *Theoretical Significance of Friedel’s Rules*

Buerger (1945) has criticized Friedel’s rules, not as being a bad description of observed facts, but as being based on lattices alone and leaving structure out of account. He concludes that these rules represent necessary but by no means sufficient conditions for twinning actually to occur. From this it would be difficult to dissent, in view of the evidence

presented in the preceding pages about the structural nature of the interface in real twins.

Figure 20, which is taken from Buerger's paper, is the key to his structural interpretation of Friedel's rules. A crystal face *P* is growing so rapidly, perhaps because of high supersaturation, that a cliff several unit cells in height is advancing across a face. (Such a cliff can be present

Fig. 20



Attachment of a minute crystallite in twin orientation at a high ledge on a growing crystal face. (From Buerger 1948.)

during 'spiral' crystal growth.) In the re-entrant corner at the base of the cliff a small crystallite or cluster of atoms arrives, already formed, and attaches itself either in parallel or in twin orientation, depending on its position at the instant it arrives. It has a reasonable chance of attaching itself in twin position if one of Friedel's rules is satisfied, for then a number of lattice points, and therefore of atoms, of the large crystals and

of the cluster will be in close proximity. Thus, if $ae_1ea'c$ represent points on the multiple Friedel lattice of the cluster, they will virtually combine with corresponding points on the cliff. If P is also the twin plane (as here drawn), there will be good fit on the tread as well as on the riser of the step. Thus the cluster can adhere in twin position if the number of atoms which fail to register at the interface between cliff and cluster is not too great. This can only be judged from a knowledge of the crystal structure. Generally, it would appear that good fit at this interface will be the more probable, the fewer atoms are associated with each lattice point.

This theory requires that a small cluster form independently and arrive at the correct position at the foot of a cliff. Clusters will only be present in large numbers if there is high supersaturation. This, together with Johnsen's ideas concerning the influence of temperature fluctuations, would account for the observed role of supersaturation in calling forth twinning (§ 2.1.3.1). The experimental evidence for the readiness, in certain circumstances, for two crystals to adhere in twin position (§ 2.1.3.3) also goes to support Buerger's ideas.

Buerger's real innovation is to make use of the partial lattice fit between twinned individuals on planes *other* than the twin plane or rhombic section, which is a direct consequence of the observance of Friedel's rules.

None of these considerations are relevant to mechanical twinning. In most cases Friedel's rules are presumably obeyed because the twin obliquity is so small that a lattice row in its sheared position is pseudo-parallel to its initial position. For those twins for which the obliquity, and therefore the shear, is large (as for instance iron and calcite) it is hard to see *why* Friedel's rules are obeyed. It would seem that only the quality of fit at the *twin plane* or *rhombic section* and the amount of shuffling of the atoms required subsequent to the shear, should affect the ease of formation of a mechanical twin, and no direct connection between these factors and Friedel's rules is obvious for twins with large shears. It would be of interest to check whether *all* those mechanical twins which have a large shear (cf. for instance the tabulation in Tertsch 1949) do in fact abide by Friedel's rules.

2.2.2. *The Origin of Growth Twins—A Difficulty*

In § 2.1.3.3 two rival views on the origin of lamellar growth twins were put forward: one supposes that stacking faults during growth give rise to the twins, the other proposes that such twins are sometimes or even always of mechanical origin. Connected with this is a further consideration which does not appear to have been widely recognized (but see Tertsch 1949, p. 132). A number of species such as the feldspars contain polysynthetic twin lamellae according to twin axis law (an axial twin), and in these cases the interface is always parallel to the rhombic section (§ 2.1.1.1). This is a geometrical plane but not parallel to any lattice

plane. Now the explanation of lamellar twins in terms of stacking faults requires that a monolayer of atoms should attach to a growing lattice plane in twinned position, but this implies that the lattice plane in question should also be the twin plane. Even supposing that by some mechanism, perhaps the arrival of a cluster of atoms as envisaged by Buerger, a nucleus of an axial twin could be established, all that can happen is that this nucleus should rapidly expand as a layer parallel to the growing lattice plane. No mechanism appears to be thinkable which would allow such a nucleus to spread along a plane not parallel to any potential growth face, and for a second fault then to complete the individual in the form of a very thin lamella. In terms of mechanical twinning of the second kind such lamellae can be effortlessly accounted for. Unless some entirely new point of view can be advanced, it seems that polysynthetic axial twins must always be put down to mechanical causes, even when such twins cannot be reproduced in the laboratory. In such cases it is necessary to appeal to the aid provided in nature by heat and pressure.

2.2.3. *Twinning and Frank's Theory of Crystal Growth*

In spite of the success which has attended Frank's theory of crystal growth by the agency of climbing spiral ledges round screw dislocations, and its ability to predict numerous observed features of crystal topography (Frank 1949, Verma 1953), it does not appear to have been extended to a consideration of the growth of twinned crystals, nor have growth spirals been searched for on twinned crystals, with one exception. Rae and Robinson (1954) have studied growth twins in lithium sulphate, and found that growth spirals sometimes extended from the tip of a thin twin lamella. The lamella and the spiral had associated growth steps of the same height. Here there is scope for further research.

§ 3. MECHANICAL TWINNING

A number of topics relating to mechanical twinning have already been fully reviewed by the writer in a recent article (Cahn 1953 c); the relevant sections have been marked with an asterisk. The treatment of these topics is here less detailed than in the other article, to which the interested reader is referred. The recent book by Hall (1954) contains good reviews of a number of the subjects dealt with here. This book, and Schmid and Boas (1935) also deal fully with some purely geometrical aspects of twinning which are omitted here.

3.1. *Experimental Facts—Crystallographic and Geometrical*

3.1.1. *Substances Capable of Mechanical Twinning*

Mechanical twinning has been recorded in some 70 different metals, minerals and compounds. The mechanical twin laws of minerals are fully listed by Tertsch (1949, p. 56), while those of metals have been listed by Hall (1953, 1954), and the reader is referred to these sources. Table 1 only gives a list of twins produced mechanically in a number of artificial

compounds, since such a table has not been published elsewhere. Twins which can only be made by heating are not included. Since the literature is extremely scattered, there can be no claim to completeness.

Hall (1953, 1954) has listed twinning elements for metallic titanium. The experimental data on which he draws only established the twinning planes (K_1), but there were no measurements from which the magnitude of shear could be computed; also the existence of three out of the five twinning laws listed is uncertain. Hall deduces the magnitude of shear and the indices of K_2 , etc., by studying atom motions graphically. In some cases the shear comes out to exceed unity. Atom motions are a highly questionable basis for predicting the macroscopic twinning elements, more particularly when the answers involve record amounts of shear. A proper experimental study of twinning in titanium is needed.

Doubts have on occasion been expressed as to the true nature of 'Neumann bands' in deformed iron and steel. They have generally been taken to be mechanical twins with (112) as twin plane and [11 $\bar{1}$] as shear direction. This has now been verified by x-ray diffraction by Kelly (1953) and by measurements of surface tilt by Paxton (1953). No doubt now remains on this score. The present writer has obtained ample crystallographic evidence for the similar genesis of twins in molybdenum.

3.1.2. *Twinning at High Temperature and Pressure*

In § 2.2.2 it was postulated that the greater ease of mechanical twinning under very high pressure and at high temperature may be quite general, and that this might justify the assumption of a mechanical origin for polysynthetic twins in minerals, even where such twins cannot normally be made in the laboratory. Here we shall summarize the available evidence.

Mügge (1886) was the first to make artificial mechanical twins under high hydrostatic pressure, in diopside and antimony. Diopside cannot be twinned in the absence of pressure, and antimony usually breaks before it will twin. Johnsen (1914) made mechanical twins in lithium sulphate by embedding crystals in flowers of sulphur and applying pressures up to 8000 atmospheres in a steel cylinder. At ordinary pressures no mechanical twins can be made, though growth twins will form, especially in the presence of potassium sulphate (§ 2.1.3.2). It would be interesting for dislocation theory of twinning to see whether growth twins made in this way can then be made thicker or thinner by applied stress at ordinary pressure.

Grühn and Johnsen (1917 a) similarly compressed rutile (TiO_2), embedded in sulphur, at 30000 atmospheres, and created twins with $K_1=(101)$, $K_2=(\bar{1}01)$, with the very large shear $s=0.908$. Rutile can also be twinned at ordinary pressure; the plane of glide is the same, (101), but $K_2=(\bar{3}01)$ and s only 0.190. The pressure has thus enabled the formation of a twin with abnormally high shear.

Table 1. Mechanical Twins in Chemical Compounds

| Formula | Crystal system | K_1 | η_1 | K_2 | η_2 | s | Remarks | Reference |
|---|----------------|-------|----------|-------|----------|-------|--|-----------------------------------|
| $\text{Na}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}^*$ | Tri | (001) | [001] | (001) | [001] | 0.018 | Twins elastically with great ease | Mügge 1930 Baumhauer 1911 |
| KHCO_3 | Mono | (001) | [001] | | | 0.119 | | Mügge 1930 |
| $\text{Mn}(\text{CO}_3\text{H})_2 \cdot 2\text{H}_2\text{O}$ | Mono | (001) | [001] | | | ? | | Mügge 1930 |
| $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ | Mono | (001) | [001] | | | 0.870 | Twinning and slip on same planes. | Mügge 1889 |
| $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ | Mono | (001) | [001] | | | 0.038 | Twins elastically | Wyrouboff 1886 Mügge 1888 |
| $\text{K}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ | Tri | (010) | [010] | (010) | [010] | 0.058 | In each case, the second type parts along rhombic section | Wyrouboff 1891 Mügge 1894 |
| $\text{K}_2\text{Mn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ | Tri | (010) | [010] | (010) | [010] | 0.188 | | |
| KClO_3 | Mono | (001) | [001] | | | 0.669 | Additional twins and 'Rose channels' are formed on heating | Mügge 1910 Madan 1886 |
| $\text{Mg}(\text{C}_4\text{H}_5\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$ | Ortho | (110) | [110] | (110) | [110] | 0.106 | | Johnsen 1907 |
| $\text{NiCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ | Ortho | (110) | [110] | (110) | [110] | 0.049 | | Johnsen 1907 |
| $\text{NiNa}(\text{UO}_2)_3 \cdot (\text{CH}_3\text{COO})_9 \cdot 9\text{H}_2\text{O}$ | Mono | (111) | [112] | | | 0.049 | | Johnsen 1907 |
| $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ | Mono | (110) | [310] | (310) | [110] | 0.128 | Twins elastically by both laws, with ease | |
| $(\text{NH}_4)_2\text{SO}_4$ | Mono | (310) | [110] | (110) | [310] | 0.038 | | Friedel 1926, p. 493 |
| | Ortho | (110) | [310] | (310) | [110] | 0.042 | | Friedel 1926, p. 493 |
| $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ | Mono | (110) | [310] | (310) | [110] | 0.002 | Twins elastically | Friedel 1926, p. 493 |
| Rochelle salt | Mono | (310) | [110] | (110) | [310] | 0.001 | Twins elastically | Chernysheva 1950, Fischer 1954 |
| BaTiO_3 | Ortho | (011) | [011] | (011) | [011] | 0.011 | Twins elastically | Kay 1948 |

(KNbO_3 , WO_3 and other ferroelectrics are known to twin but detailed studies remain to be made.)

* Brasseur and de Rassenfosse (1941) have shown that many complex cyanides of the alkali metals, with anions containing Pt, Pd or Ni, are all isomorphous with each other and twin according to the same law as sodium platinocyanide. It is not known whether the twins can be made mechanically in these other compounds.

If the temperature is raised as well as the pressure, twinning is further facilitated. Thus Heide (1931) made twins with $s=0.7$ in baryte, BaSO_4 , by compressing to 16 000 atmospheres at 400°C or above. High pressure at 300°C , or heating to 1100°C in the absence of a high hydrostatic pressure, failed to generate the twins. Seifert (1928) postulated that the twin lamellae in galena, obviously mechanical in origin, were found in nature at high pressure and temperature.

Dolomite is known to twin on $(0\bar{2}21)$ (e.g. Fairbain and Hawkes 1941), though not on $(10\bar{1}2)$ because of the presence of crystallographic order (§ 1.3.3). Calcite twins very easily on $(10\bar{1}2)$, but not on $(0\bar{2}21)$ even though its structure is similar to that of dolomite. At high hydrostatic pressure twins on $(0\bar{2}21)$ can be made (Turner and Ch'ih 1951); however there is some slight doubt whether twinning or slip is involved.

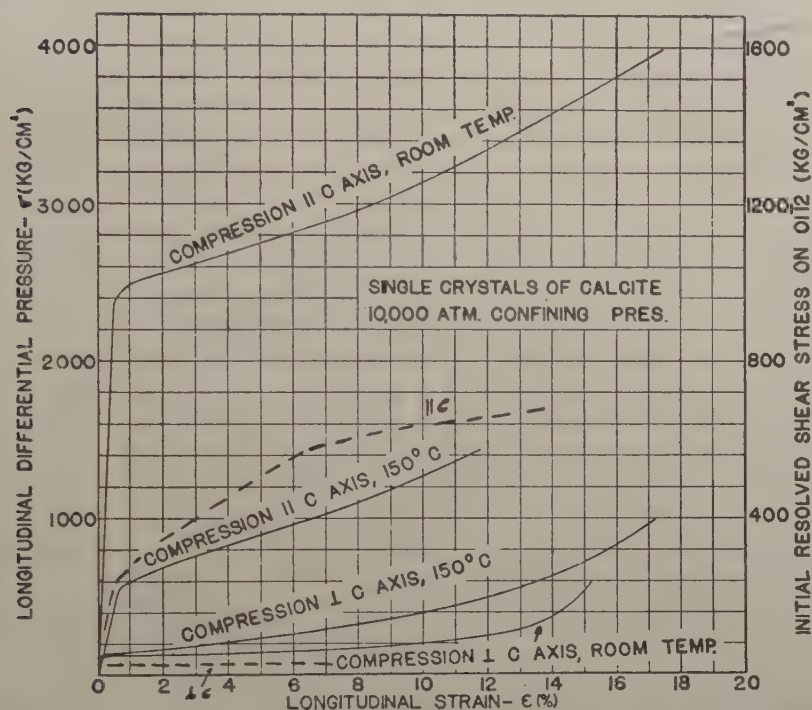
In titanium, it has been found that the relative frequency of the several distinct twinning laws is radically altered as the temperature is raised (McHargue and Hammond 1953).

Not only does high pressure sometimes call forth twins which cannot else be made, but it may allow more profuse twinning in substances which are in any case liable to it. This was shown for instance by Griggs and Miller (1951) in experiments on marble (polycrystalline calcite) deformed at 10 000 atmospheres pressure.

It is a well established rule in metallurgy that as the temperature is raised, slip is favoured at the expense of twinning, to the point where twinning may cease altogether. This has been established for zinc and cadmium (Schmid and Boas 1935, Ramsey 1951), iron (Pfeil 1926, 1927), beryllium (Kaufman *et al.* 1950, Hausner and Pinto 1951), uranium (Cahn 1953 a) and molybdenum (Cahn, unpublished work). In the case of magnesium there is a difference of opinion, since Bakarian and Mathewson (1943) recorded an increase in twinning with rise of temperature, but Barrett and Haller (1947) and Ansel (1948) observed an opposite tendency. The stress necessary to produce either slip or twins falls as the temperature is raised. The rule referred to cannot therefore be taken as evidence that twinning becomes more difficult at higher temperatures, but only as showing that the stress needed for slip varies more sharply with temperatures than does the twinning stress. This interpretation has been extensively confirmed in the elegant experiments on hydrostatically compressed marble carried out by Griggs *et al.* (1951, 1953). These authors showed by orientation studies that slip on $(10\bar{1}1)$ and $(0\bar{2}\bar{2}1)$ must occur extensively at high pressure. Comparative tests at room temperature, 150°C and 300°C showed that slip gained at the expense of twinning as the temperature was raised; more precisely, the critical stress for slip falls steeply. (Full data concerning slip in calcite are to be published by Turner, Griggs and Heard 1954.) By using a machine from P. W. Bridgman's laboratory, Griggs and his co-workers were able to obtain stress-strain curves for calcite single crystals under 10 000 atmospheres pressure (fig. 21). A crystal compressed along the c axis can only slip, while one compressed at right angles to this direction can only twin.

The curves reproduced in fig. 21 thus indicate the resistance to the two modes of deformation at the two temperatures, in the presence of a large superimposed hydrostatic stress.*

Fig. 21



Stress-strain curves of calcite single crystals under high hydrostatic pressure.

The dashed lines have been added from data supplied by Dr. Griggs.

They represent experiments at 300°C. (From Griggs *et al.* 1951.)

3.1.3. Influence of Purity

Very little is known about the influence of composition or constitution in the metallographic sense, on mechanical twinning. Silicon, aluminium and other impurities are known to favour twinning at the expense of slip (e.g. Barrett, Ansel and Mehl 1937); this is probably to be taken in the sense that the resistance to both is raised, but unequally. Apparently tin twins more readily when pure. Thus Biringuccio (1540) asserts that the purity of tin may be estimated by biting a thin piece and listening for the characteristic cry. This opinion is also to be found in the 1948 edition of the *Metals Handbook*.† Tests by the present writer with tin containing substantial amounts of added impurity do not bear out the statement. Nothing whatever is known about the effect of precipitates or age-hardening zones, eutectic structures, etc. A fine grain-size always raises the resistance towards twinning.

* Griggs (private communication) states that the 150°C curves in this figure are somewhat in error owing to the presence of cleavage cracks. The 300°C curves are based on unpublished experiments.

† The matter has been further discussed by R. P. Lister, 1954.

3.1.4. *Twinning and Slip*

3.1.4.1. *Twins of the Imagination.*—The term used as title for this section was coined by Friedel to express his disapproval of the numerous twin laws reported in mineralogical literature which did not meet the basic requirements of rational twin elements and exact reproducibility. Twins of the imagination can also be generated mechanically.

The most persistent 'twin law' of this kind is that reported in rocksalt crystals which had been compressed. The reason for dismissing the possibility that the lamellae obtained are really twins is that the surface tilt of a crystal face varies within wide limits, which means that the shear and twin obliquity vary correspondingly. For a genuine twin these *must* be fixed. The experiments in question were done by Brilliantov and Obreimov (1935, 1937), Brilliantov and Startsev (1939) and Startsev (1940). The true nature of the lamellae has been established by Pratt (1951), who showed them to be due to kinking, which is a variant of the slip process. Kinking has been observed in numerous crystals, in particular metals, ever since the original discovery of the process in barium bromide (Mügge 1889). An understanding of the process is only possible in terms of dislocations, and since these were unknown in 1889 Mügge took his deformed crystals to be twinned. Friedel (1926) referred to kinks as 'pliages en genou', and gave an account, not very intelligible, of how he supposed them to have been formed. Kinking has been particularly well studied in zinc (Hess and Barrett 1949). It continues to be observed also in non-metals; thus Chudoba and Frechen (1950) have carefully documented the kinks they observed in olivine $(\text{Mg, Fe})_2\text{SiO}_4$, which they distinguished from twins; Turner, Griggs and Heard (1954) have studied kinks in calcite. However, Berg (1934) observed 'mechanical twins' in bismuth, with (751) as twin plane. Converted to the conventional Miller-Bravais indices, this is (2241), which is almost normal to the slip direction [1120]. The interfaces developed during the kinking process always start by being normal to the slip direction and then slowly deviate from this position. Since in addition Berg noted that the amount or shear was variable, it is evident that he had really observed kinking. Incidentally this is relevant to the argument current in metallurgical literature as to whether bismuth is capable of slip.

Many attempts have been made to detect mechanical twins in face-centred cubic metals, but even the most thorough searches (Mathewson and van Horn 1930, Burke and Barrett 1948) have failed to find any trace of such twins. Elam (1928) observed regions in what she took to be twinned orientations in stretched aluminium crystals, but Rybalko and Yakutovich (1948) showed that these islands of special orientation were a product of slip and resulted from the special orientations of the crystals used.

3.1.4.2. *Twinning and Slip on the Same Crystal Plane.*—Several instances are on record of twinning and slip occurring on the same lattice plane. Thus iron and molybdenum twin on (112) and probably (112) is one of the possible slip planes, though this is still a point at issue (Chen and Maddin

1951, Brick and Steijn 1954). Again, monoclinic barium bromide (Mügge 1889) forms mechanical twins with $K_1=(100)$; but if a shear stress is applied to (100) in the reverse sense, slip takes place on the same plane, while loading in a different way leads to kinking through the operation of this same slip system. Here the sense of shear for slip and twinning are opposite, but in potassium chlorate (Fischer, quoted by Friedel 1926, p. 500) slip and twinning occur in the same sense. (Slip is only possible in one sense because these crystals possess no centre of symmetry.) As Friedel points out, in barium bromide the 'shear to identity' (i.e. the slip shear) exceeds the twinning shear, while in potassium chlorate the twinning shear is the greater. Correspondingly, slip is easier in potassium chlorate and twinning is easier in barium bromide.

These crystallographic curiosities should certainly be taken into account in any general treatment of twinning in terms of dislocations.

*3.1.5. *The Shapes of Mechanical Twins*

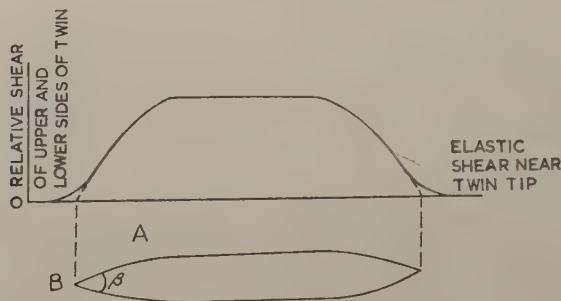
The scheme of mechanical twinning presented in connection with fig. 11 leads to a twin consisting of two individuals separated by an interface parallel to the plane of glide. The scheme is easily adapted to yield a parallel-sided twin lamella; it is only necessary to start with an infinitely thin twinned nucleus, instead of initiating the twin at the free surface. In this case the lamella would have to go right through the specimen. In practice, and particularly in the realm of metallurgy, twin lamellae are not parallel-sided and do not traverse the specimen. If a twinned piece of metal is sectioned and etched, the lamellae are seen to be lens- or cigar-shaped in cross section, and the spread of any one lamella is most often restrained by impingement on another lamella formed by the operation of a different plane of glide. Yakutovich and Yakovleva (1939) examined the shape of such lamellae inside a zinc crystal in three dimensions by repeated sectioning. The shape is that of a biconvex lens greatly stretched out in one direction normal to the optic axis. This direction is normal to the direction of shear. The lamella is usually thin when measured in a direction normal to the plane of glide, though in some metals, as bismuth, this may not be so. A lamella of this sort may be thought of as consisting of many elementary parallel-sided lamellae of different areas placed in contact with each other. Since each such elementary lamella contributes to the relative shear of the upper and lower portions of the residue of the original single crystal, this shear varies from point to point in the way sketched in fig. 22. The strain discontinuity at points such as A is due to the presence of a twinning dislocation (§ 3.5.2), while that at B is partly relieved by a slip manifestation, called accommodation bending (§ 3.1.6).

It appears that the angle β (fig. 22) can exceed a few minutes of arc only if the substance is capable of slip and therefore of accommodation bending. Most minerals cannot slip and correspondingly twin lamellae in minerals are observed to be parallel-sided. Unless the twin thickness is of the order of a micron or less, such lamellae, unless they go right through the crystal, may be terminated by an area of cleavage (§ 3.1.6).

3.1.6. *Twin Accommodation*

3.1.6.1. *Accommodation Fracture*.—The term *twin accommodation* was introduced by Jillson (1950) to describe the plastic configuration which relieves the strain discontinuity at the edge of a lens-shaped twin lamella. It is here extended to cover fracture at the lamella edge.

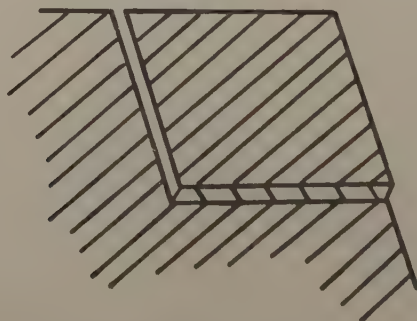
Fig. 22



Variation of shear strain across a lens-shaped twin lamella.

Rose (1868) was the first to study fracture of this sort in pieces of calcite twinned either by nature or by man. Wherever any but the thinnest of lamellae stopped inside a crystal, a cleavage crack extended for some distance from the lamella edge, as sketched in fig. 23. This

Fig. 23



Cleavage at the termination of a twin lamella in calcite.

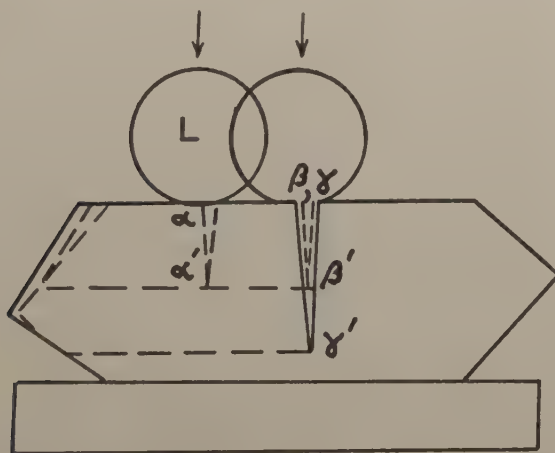
applied only to the leading edge of the lamella (the edge normal to the shear direction). An edge roughly at right angles to this was apparently able to accommodate the strain discontinuity elastically. Where two lamellae parallel to different planes intersected, a hollow channel, now termed a *Rose channel*, was formed.

Mügge (1888) observed somewhat similar fractures in barium chloride, but these had the extraordinary capacity of moving through the crystal

as the twin increased in extent. The upper left part of the crystal in fig. 24 has been twinned. $\alpha\alpha'$, $\beta\beta'$, and $\gamma\gamma'$ represent successive positions of one boundary of the twinned portion; the other boundary is always parallel to the plane of glide. As the loading cylinder L was rolled from $\alpha\alpha'$ to $\beta\beta'$, the twinned portion expanded and the bounding crack advanced with it. Then, the pressure was increased and the twinned portion thickened, the crack with it to $\gamma\gamma'$. The crack is bounded by faces parallel to (100) in the two individuals. Positions such as $\alpha\alpha'$ where the crack had briefly remained stationary were marked by a faint inclusion of air, which prevented complete healing of the crack. If the crystal is untwinned again by loading in a different direction, these ghost cracks remain and the crystal frequently fractures at one of these sites.

If very thin lamellae are made in calcite or barium chloride, by loading with an edge or a point, no cracks appear and the twins disappear again on relaxing the load (see § 3.2.3). Once cracks appear, the twin lamellae become locked in position.

Fig. 24



Accommodation fracture associated with a twin in barium chloride.
(After Mügge 1888.)

3.1.6.2. Accommodation Bending.—Figure 25 (a) is a cross section of a wedge-shaped twin lamella in zinc terminated by an accommodation bend (exaggerated in the figure). This is a sub-boundary within the main crystal, approximately normal to the slip direction $[11\bar{2}0]$, and dividing the crystal into two portions with orientations differing by a rotation about an axis normal to the slip direction and lying in the slip plane (0001). The angle is quite closely constant, being about $45'$ in zinc. The configuration is deduced from microscopic examination of the cleavage surface, making use of modern techniques for detecting small surface tilts. The main studies are by Jillson (1950), Pratt and Pugh

evidence has accrued from a study of twins in titanium (Rosi, Dubé and Alexander 1953).

If this is correct, then ϕ is constant if γ , the angle between twin lamella and bend plane, is constant. Since this is roughly the case for the different hexagonal close-packed metals, it is predicted that ϕ should be approximately constant for these metals.

For zinc, substituting for known quantities in eqn. (1), a value of $\sim 4^\circ$ is computed for β . This angle can also be estimated from photomicrographs showing both twin lamella and accommodation bend. The lengths of BC and CF are measured on the micrograph; BE and hence β can then be calculated. From an exceptionally clear photograph taken by W. D. Biggs (private communication) β is obtained to be $4\frac{1}{2}^\circ$.

Ancker (1953) showed that there was a fine substructure in the vicinity of one of the two interfaces of a twin lamella in a zinc crystal, which she presumed to be an accommodation phenomenon. The origin of this substructure is not yet understood; the observed orientations of the subgrains preclude polygonization (e.g. Conard, Averbach and Cohen 1953) as an explanation.

Although detailed studies of accommodation bends have been restricted to zinc, there is little doubt that much the same configuration is to be found in other metals such as cadmium, bismuth, uranium. All these metals are known to be capable of kinking, which is basically the same process as the formation of accommodation bends. It is certain that metals such as those cited owe their facility in twinning to their concurrent ability to form such bends; in the absence of this ability, only extremely thin lamellae could arise and the material would soon fracture. In more general terms, the ability to slip accentuates the ability to twin.

3.1.7. *Twin Intersections*

A twin lamella parallel to one plane generally acts as an impenetrable obstacle to a lamella parallel to another, though the shock of impact of the one on the other frequently produces a fresh lamella on the far side of the obstacle. In special circumstances, however, one lamella can pass smoothly through another. The conditions for this to be possible have been investigated by Cahn (1953 a). The lamella being crossed (i.e. the one formed first) must be formed by twinning of the first kind and the shear direction operating in the crossing lamella must be parallel to the line of intersection of the two lamellae. A secondary twin is formed within the lamella being crossed and this links up without any stress concentration with the crossing lamella, if these conditions obtain. A detailed account will be found in the paper cited. Such intersections have been found in twinned meteoric iron (Smith, Dee and Young 1928) and copiously in uranium (Cahn 1953 a). By allowing two sets of lamellae to be formed without mutual interference, the capacity to form such true intersections facilitates deformation by twinning. Pratt (1953) has shown that intersections are sometimes found in zinc, although here the specified conditions are only roughly obeyed.

In iron, and the other body-centred cubic metals, the twelve $\{112\}$ twinning planes are divided into four groups of three each having a common shear direction $\langle 111 \rangle$. Since twins in iron are of the compound variety (§ 1.2.2.2), the shear direction is also a twin axis. Consequently lamellae parallel to *any* of the three $\{112\}$ planes in a group are all converted to the same orientation by the twinning operation, and they can also form true intersections with each other. The common orientations of such lamellae have been confirmed by examining polished and etched sections of meteoric iron (Cahn, Brown and Clare, unpublished work). Two intersecting lamellae parallel to (121) and $(21\bar{1})$ were seen to be continuous in the sense that etching brought up no boundary between them.

3.1.8. *Strain at the Twin Interface*

There is much evidence that the interface between a twinned lamella and the grain from which it originated is in a highly strained condition, in contradistinction to the good fit and low specific energy at the interfaces of growth and annealing twins (§§ 1.3.1 and 2.1.1.4). Mechanical twin interfaces are preferentially etched, both chemically (Mügge 1932, Zolotov 1943) and by simple heating (Cahn 1953 a). Sensitive x-ray diffraction has revealed considerable distortion in the vicinity of the interface in iron (Barrett 1945) and in zinc (Ancker 1953). Ancker measured the very large difference of 0.3% in the a parameter of the material either side of the interface. However, the strain was apparently localized only at one of the two interfaces of each lamella. The readiness to fracture (§ 3.1.9) and to recrystallize (§ 3.3.3) at the twin interface is also evidence for a state of high strain. For reasons mentioned before (§§ 2.1.1.5 and 2.1.1.6) twin lamellae in tin are known to be exceptional in not being noticeably strained.

Partly the high strain must probably be put down to the dislocations necessarily present at the interfaces of lens-shaped lamellae, but this cannot be the whole explanation, because the interfaces of twin lamellae in iron are fiercely attacked by chemical etchants although they are often very nearly parallel-sided. This behaviour is in sharp contrast with the resistance to etching of the artificially induced (112) interface of an annealing twin in iron (§ 2.1.1.4). Experiments by the writer have shown that the interfaces of mechanical twins in iron continue to etch readily even after a long anneal at 900°C . Perhaps the thickness of mechanical twin lamellae fluctuates on a submicroscopic scale so that the density of dislocations is larger than is apparent. More quantitative data on interface energies of mechanical twins are needed before a proper understanding of the interface strain can be looked for.

*3.1.9. *Twinning and Fracture*

Two types of fracture are observed to be specifically associated with mechanical twins: *accommodation fracture* (§ 3.1.6.1) and *parting* along one of the interfaces.

An unusually complex form of accommodation fracture was studied in zinc by Yakovleva and Yakutovich (1950). Zinc crystals were

compressed in a direction parallel to the hexad axis. This form of stressing permits twinning but does not favour kinking, and therefore accommodation by fracture is preferred. The crystals contain staircases of narrow lamellae separated by short cleavage cracks, which are bounded by $(10\bar{1}0)$ in the crystal and (0001) in the lamellae. The cleavage is so extensive that the density of the crystal diminishes considerably. Again, iron and steel are liable to accommodation fracture under impact, though the evidence is scanty and controversial. Thus Tipper and Sullivan (1951) recorded that cleavage cracks often originated at the edges of twin lamellae and spread along a plane at a small angle to the interface.

Parting along twin interfaces in stressed crystals (the term is of mineralogical origin) is firmly established by numerous instances scattered in mineralogical literature. In calcite the fracture follows the interface very precisely, as shown by accurate goniometric measurement (Březina 1880). Under the microscope such a fracture surface shows no features even under the highest magnification (Cahn, unpublished work). In metals, particularly relatively brittle ones, parting has also been observed. Particularly clear and convincing photomicrographs have been published of partings in antimony, by Zapffe (1953, figs. 29 and 33). Parting has also been observed along (112) twin lamellae in molybdenum compressed by impact in liquid air (Cahn, to be published). No clear evidence of parting in iron has been published, though much controversy has raged on the matter. That parting takes place along the interface rather than along a specific lattice plane is shown by the fact that it can occur along the interfaces of twins of the second kind, which are not parallel to lattice planes. This has been verified in potassium cadmium sulphate (Mügge 1894), and in uranium (Cahn 1953 a).

It has been proposed that the overall fracture of a stressed crystal or polycrystalline specimen may be triggered by parting or accommodation at a twin lamella, but this is still very much under debate. Some clear microscopic evidence has been obtained by R. L. Bell of fractures in zinc crystals starting at the points of high stress concentration where pairs of twin lamellae on different planes abut on each other (to be published), and the correlation between fracture and twinning in compressed molybdenum crystals observed by the writer points the same way. Some hold that twins in iron and steel are a main cause of fracture (e.g. Bruckner 1954), but on the other hand it is clear that twins are observed without fracture and fracture without twins (e.g. Geil and Carwile 1953, Rosenthal and Woolsey 1952). Low and Feustel (1953) have published some excellent photomicrographs which suggest that in pure iron twins form only immediately beside an advancing crack, but in carbonized iron they can form previous to fracture. Probably no generalized answer is possible.

Derruyttère and Greenough (1954) have recently carried out elegant experiments with zinc crystals, comparing in detail the two fractured surfaces and correlating the direction of crack propagation with the observed twin lamellae. The evidence strongly supports the view that here the spreading crack nucleates twins (*not vice versa*) because of the

stress concentration ahead of the crack. Bilby and Bullough (1954) have interpreted these observations in detail.

Evidently it is too early as yet to draw any firm conclusions about the inter-relation of twinning, fracture and slip. Perhaps the following tentative argument is at any rate not in conflict with the published facts : A twin can only be created by a powerful concentration of stress (cf. § 3.2.5) and it is generally admitted that a localized stress-raiser is needed to create a cleavage crack. There is some evidence that a pile-up of slip dislocations can produce the stress-concentration needed to start a twin (Bilby and Entwisle 1954) ; it has been proposed that such a pile-up can also trigger a cleavage crack (Petch 1953). A certain symmetry is discernible in the complex of theory and observation. The following sequences of events are *a priori* feasible in an externally stressed specimen : (a) A pile-up of dislocations at a terminating slip band triggers a pair of twins, along whose line of junction a cleavage crack is then created. The crack spreads because of the applied stress. The spreading crack may or may not create further twins on its progress. (b) A pile-up of dislocations at a terminating slip band directly creates a fracture, which may create twins as it spreads. In either case (a) or case (b), the spreading crack may encounter existing twins (themselves possibly triggered by the initial twins which created the crack in the first place) ; if so, the crack may be deviated on account of localized parting at the twin interface.

Because of the manifold possibilities listed, it is not to be wondered at that no single sequence will account for all the published observations.

3.1.10. *Twinning and Deformation Textures*

When polycrystalline metal is intensively deformed, it acquires a texture—all grains approach a uniform orientation. Numerous attempts have been made to interpret the final texture in terms of the known crystallographic features of slip in the various metals, with a fair degree of success. It has also proved possible to incorporate the discontinuous reorientation brought about by twinning in theories of this kind. Thus Calnan and Clews (1950, 1951, 1952) have interpreted the rolling textures of hexagonal close-packed metals and of uranium to a first approximation, making use of the known twinning crystallography of these metals. Somewhat arbitrary assumptions about the relative ease of slip and twinning are necessary.

Griggs and his co-workers have achieved a very detailed interpretation of the textural changes in marble (polycrystalline calcite) compressed under high superimposed hydrostatic pressure. The initial texture (due to geological causes) was accurately known and calculations were made for individual grains each of which had a known initial orientation, which allowed more precise predictions than Calnan and Clews' method of postulating a random starting texture. The relative ease of slip and twinning were estimated from experimental stress-strain curves. All attempts to account for the observed compression textures on the basis of a 'heterogeneous' hypothesis, as also used by Calnan and Clews,

failed badly. 'Heterogeneous' in this connection implies that all grains behave as if they were not constrained by their neighbours, so that only those favourably oriented for slip or twinning are deformed. By applying Taylor's 'homogeneous' hypothesis that all grains shared equally in the deformation, undergoing mainly slip or twinning according to orientation, very good agreement between predicted and observed textures was attained. This is the first time Taylor's hypothesis has been verified by textural studies (Griggs and Miller 1951, Handin and Griggs 1951, Turner and Chi'h 1951, Griggs *et al.* 1951, 1953).

3.2. *Experimental Facts—Dynamic*

*3.2.1. *Does a Maximum Resolved Shear Stress Criterion Apply to Twinning?*

In all metals slip is subject to a well-defined critical shear stress, resolved in the slip plane and direction, which determines at what applied stress slip starts and which of several alternative slip planes operates. The existence of such a criterion has repeatedly been proposed for twinning, but it has never been convincingly demonstrated. It has been fairly well established that the most highly stressed twinning plane operates out of several alternatives, though exceptions have been recorded even to this. Thus W. D. Biggs (private communication) working with iron crystals found that two or more sets of lamellae often form simultaneously, of which one set may actually be oriented to cause compression though the crystal had been pulled. In cadmium the most highly stressed twinning plane was always found to operate (Thompson and Millard 1952) and Griggs (1938) found the same for calcite crystals. R. L. Bell (private communication) has confirmed this for zinc, and the writer (unpublished work) has confirmed it for molybdenum. Lee and Brick (1953) have shown that in compressed beryllium crystals that twin plane operates which provides the greatest contraction of the specimen in the direction of compression. This is also the most highly stressed plane.

The existence of a critical stress must be doubted for two reasons. Firstly, different investigators using material of similar purity obtain quite different values for the 'critical stress', and secondly this value in any one series of experiments usually has a large scatter. Thus for cadmium, room temperature values of 140 ± 40 , 420 ± 50 and 50 ± 25 g/mm² have been recorded, respectively by Thompson and Millard (1952), King, Gumbell and Makin (to be published), and Yakovleva and Yakutovich (1940). Again, for zinc, Davidenkov *et al.* (1939) obtained values in the range 400–600 g/mm² and Miller (1936), 300–650 g/mm². However, Bell and Cahn (1953), using crystals of an orientation slip which excluded slip, and loading them with many precautions, were usually able to apply a resolved shear stress of 3000 g/mm² without producing any twins. These experiments make it seem highly probable that most investigators have measured stresses required to thicken already existing twins, which might start by being very small.

Whether the divergence of results for cadmium, for instance, was due simply to accidental distortion of the crystals in some cases, or to different purity or surface condition, can only be guessed at.

The surface condition is particularly liable to affect the range of stress at which twins begin to form. King (1952) has shown that this range is raised when cadmium crystals are oxidized on the surface, and Gilman and Read (1952) have observed a large rise of resistance to twinning when a thin layer of copper was plated on to zinc crystals. Vogel and Brick (1953) and Steijn and Brick (1954) have examined twinning stresses for pure iron and have concluded that there is no critical resolved shear stress. Krafft, Sullivan and Tipper (1953) have evidence that there is such a stress.

It is well known that existing twins can be gradually thickened or be made to disappear by slowly changing the applied stress, but the initial appearance of a twin is always sudden. When a beam-loading machine is used, the stress falls greatly even while the twin is growing. This goes to show that large local stress concentrations are needed to start a twin growing to visible dimensions, but that once the energy barrier, whatever it may be, has been overcome, the twin can grow much more easily. The necessity for local stress concentrations would not be consistent with a critical applied stress criterion. Evidence for this picture will be presented in the following pages.

3.2.2. *Rapid Initial Growth of a Twin Lamella*

The evidence usually adduced for the rapid growth of twins is the *twinning cry* emitted by a metal such as tin or zinc, which has been familiar to metallurgists for centuries. In favourable cases it can be heard across a room. More precise tests have confirmed the evidence of the ear. Thus Förster and Scheil (1940) recorded the associated changes in electrical resistivity on an oscilloscope screen and found that pulses, associated with the growth of individual twins, were completed within a time of the order of 10 microseconds. Mason, McSkimin and Shockley (1948) made similar observations with tin, but using the piezoelectric response of a quartz crystal which was in contact with the tin. Both experiments revealed a train of small waves following the completion of the pulse, which were probably genuine and not due to the apparatus. They could be due to small periodic alterations in thickness of the lamella.

*3.2.3. *Elastic Twinning*

Mügge (1888) in his investigation of twinning in barium chloride observed that a needle, pressed gently into a crystal, generated twin lamellae which disappeared when the pressure was relaxed. This is *elastic twinning*. When the pressure was too great, some of the lamellae remained; these are *residual twins*. Twins also attended the *local* heating due to a glowing platinum wire which was made to touch a crystal, and these also disappeared when the crystal cooled. A number of other crystals are now known to be liable to elastic twinning. These are indicated in table 1. In addition to these, graphite is now known to

form mechanical twins (Laves, private communication), and these are reversible with stress, which is no doubt the reason why they have been so long before being discovered. Laves' recent work (1952) has also shown that heat-treated (disordered) albite twins elastically.

The writer has examined for himself the formation of mechanical twins in nickel sodium uranyl acetate, first discovered by Johnsen (1907). It is spectacular. A crystal can be filled with hundreds of lamellae parallel to two different planes, by gently pressing two of its faces between hard surfaces. On relaxing the load, the lamellae generally disappear gradually over a period of several seconds. Albite is harder to twin, and it is necessary to apply a large force with a needle; here again there is a time delay before the lamellae have disappeared.

Chernysheva (1950) observed elastic twinning of a different kind in Rochelle salt. Fine lamellae twins were already present as a result of a phase transformation (§ 2.1.5.4). When a glass ball was pressed into a crystal, the twin lamellae in the area of contact, as seen under a microscope through the ball, were affected. The area became divided into quadrants, in two of which lamellae of the one orientation became thicker, while in the other two the lamellae of the other orientation were thickened. This thickening increased as the stress was raised, and disappeared when the stress was relaxed. If stressing was carried to the point of inducing cracks, the twins stayed thick when the load was removed ('stopped' elastic twins, cf. next section). This observation has been independently made by Fischer (1954).

**3.2.3.1. Elastic Twinning of Calcite and Sodium Nitrate.*—The most thorough study of elastic twinning was made by Garber (1938–1947). He cut specimens out of cleavage rhombohedra of calcite or sodium nitrate so that the cut surface was normal to a shear direction. The artificial surface was then loaded, either through a convex lens or else through a hard knife-edge set on the crystal parallel to the trace of the expected twin lamella. The purpose of the lens was to permit the taking of photomicrographs containing interference fringes by reflected light, which revealed even the thinnest twins because of the associated surface tilt. Garber found that at a certain load a short, very thin twin lamella suddenly appeared, grew longer and thicker as the load was increased, and shortened and finally disappeared on relaxing the load; the lamella did not begin to shorten until the load was reduced well below the value at which it was reversed. In this experiment, the crystal was viewed by transmitted light whilst being dead-loaded through the knife-edge. The 'critical' load was so small that Garber thought the twin might have started to form, though too small to see, at the smallest loads.

A. J. Williams and the writer have built a device by means of which a measured load, continuously variable, was applied to the crystal through a convex lens, so that the length of the lamellae could be accurately measured at any load from the discontinuities in the interference pattern.

This more sensitive method showed that the elastic twin appears suddenly after the load has been increased for some time, that its length *increases in discrete steps* as the load is *smoothly* increased, and that the decrease in length (again stepwise) and final disappearance, on unloading, take place at lower loads than during the loading half of the cycle. A faint trace sometimes remained visible on the surface after the load had been entirely removed, and on reloading the twin reappeared at the same place. In successive cycles the size of the jumps in length, and the degree of load hysteresis, steadily diminished. The twins were all well under one micron in thickness. The first jump remained large, and the load/length plot approximated to a straight line which could be extrapolated back to the origin.

Garber also found that an elastic twin sometimes did not disappear entirely but remained stable, perhaps after contracting part way. This he termed a *stopped elastic twin*. He attributed to the presence of micro-cracks near the loading edge, or else to the distortion of the lattice by slip (the feasibility of which he postulated). This idea is supported by the observation that stopped elastic twins were much more common at high temperatures, because it is now known (§ 3.1.2) that calcite slips readily when hot. Williams, whose tests were restricted to room temperature, confirmed that a small cleavage crack immobilized a twin which had behaved elastically until it reached the crack. Garber noted that repeated load cycles sometimes dislodged the obstacle, releasing the stopped twin.

Garber further observed that when an elastic twin is loaded far enough, it suddenly spreads across the whole cross section of the crystal, becoming parallel-sided where before it was wedge-shaped. If the elastic twin was a stopped one, this spread would be effected by means of a *distributed* load. The twin is now a residual twin, because removing the load does not cause the twin to contract or disappear. A residual twin could often be removed, however, by applying a large reverse load. When the temperature was lowered to that of liquid air, the elastic limit was raised so much that the crystal broke before the twin could become residual.

Once a twin was residual, further loading *at stresses below the elastic limit* would cause it to become thicker, while remaining parallel-sided. It could at any time be made thinner again by applying a reverse load of the same magnitude as the forward load which had been applied before reversal. This is formally analogous to plastic extension and compression in the absence of a Bauschinger effect.

3.2.3.2. Elastic Twinning in Ferroelectrics.—Apart from Chernysheva's observations on Rochelle salt, elastic twinning has also been observed in Rochelle salt and potassium dihydrogen phosphate by Mitsui and Furnichi (1953). The thickness of twin lamellae altered in a stepwise fashion as an applied electric field was altered in intensity. When the field was reduced, there was a hysteresis in the response. According to E. A. Wood (private communication) barium titanate is also subject to such hysteresis.

3.2.3.3. *Absence of True Elastic Twinning in Metals.*—Williams attempted to make reversible (elastic) twins in a zinc crystal by loading a surface, cut by a strain-free method and normal to a shear direction. Neither loading with a lens nor with minute steel balls ever produced anything but stable twins, though these might be very small. They were always wedge-shaped, and their thickness again increased in discrete steps. It seems then that in zinc, and indeed probably in all metals, elastic twins are always 'stopped' by slip interference. Gindin and Startsev (1950), in their study of the twinning of bismuth, never found any elastic twins in spite of the reluctance of bismuth to deform by slip. They were able to make parallel-sided twins traversing the specimen as in calcite. A peculiar form of elastic twinning has, however, been observed in certain alloys (cf. § 3.2.7).

3.2.3.4. *Critical Loads and Elastic Limits.*—A range of values was quoted by Garber in his various papers; for a detailed review see Cahn (1953 c). The figures for the elastic limit were computed over the whole specimen section and have therefore little meaning, since, as Garber established by means of experiments with knives of various dimensions and materials, *concentrated* loading was essential for making elastic twins. The true local stress was therefore much greater than the figures quoted, which are of the order of 200 g/mm². 100 g/mm² or less sufficed to thicken a residual twin. The disparity of two to one between these stresses is really a crude underestimate, for this latter process is in fact determined by the distributed load right across the crystal and not by the large local stress near the knife edge, or point of contact of the lens.

3.2.4. *Influence of Crystal Perfection*

Garber, Zalivadny and Startsev (1947) tested sodium nitrate crystals with various degrees of substructure or macromosaic. Those with a well-developed substructure (angular range of orientation about 1°) never formed residual twins (elastic twins were apparently not looked for), while those with little substructure formed thick residual twins. Williams found that a crystal of calcite which had crystallized imperfectly to judge by the lack of uniformity of the cleavage, would not even twin elastically.

3.2.5. *Twin Nucleation*

As the preceding sections will have made clear, three entirely distinct stages are involved in the generation of a twin lamella. A large *local* stress creates a small lamella; an increase of this *local* stress may cause the lamella to grow elastically, until it becomes unstable; a smaller *distributed* stress then causes the twin to thicken.

Bell and Cahn (1953) obtained direct evidence for the necessity for localized stressing in twinning zinc crystals. Crystals with the basal plane parallel to the crystal axis (and therefore incapable of slip) could be fractured at high stresses without twinning, except sometimes at the

instant of fracture. If, however, a small indentation was made in the crystal while it was under a sufficiently high stress (about 2 kg/mm^2 , resolved), a tremendous burst of twinning resulted. The high local stress under the indenting knife edge had produced some small twins which were then able to grow under a distributed stress which had not been able to initiate them. However, if the indentation was made first and load applied after, the small twins so produced would not grow but generally remained unchanged when the specimen broke. The growth of the twins created in the first of these experiments was terminated only because the loading beam unbent and relaxed the load. Subsequently a smaller load ($0.3\text{--}1.0 \text{ kg/mm}^2$) sufficed to make the existing twins thicker.

Slip can provide the stress concentrations necessary to initiate a twin lamella. When a zinc crystal had been slightly bent before pulling, large twins were formed at tensile stresses about equal to the stress which had been needed for indentation to trigger a twin avalanche. Bilby and Entwisle (1954) have proposed a mechanism for stress concentration through slip (§ 3.5.2).

Ancker (1953) has obtained good evidence for the necessity of localized stress. In the course of precision measurements of lattice parameters of single crystals of zinc she found that a thin surface layer of a crystal grown in a glass container was often highly strained. Weeks after the crystal was made, a twin might suddenly appear on the crystal. In the vicinity of the twin the lattice parameter of the crystal was back to normal. The parameter measurements indicate that the stress in the surface layer was of the order of 100 kg/mm^2 before the twin formed. The relaxation of this stress also led to the formation of the unexplained array of subgrains in the vicinity of the twin to which reference was made before. Thompson and Millard (1952) have also encountered delayed twinning in cadmium held under tension at room temperature, but did not find it at the temperature of liquid air.

The behaviour of zinc, then, is quite closely similar to that of calcite. The important differences are these. Small twins made by local loading will not disappear; they are all 'stopped' elastic twins. Both in calcite and in zinc a stopped elastic twin can be made to grow by applying a distributed load *or* by increasing the local load. A distributed load, if large enough, causes a sudden and spectacular growth, under continuously *falling* stress if a loading beam is used; in the case of zinc only, an *avalanche* may result, i.e., the spreading twin triggers the appearance of many new twins. An increase of local load causes *sudden* spreading of a twin only in calcite; in zinc the twin spreads slowly (i.e., it remains a stopped elastic twin), and concurrently slip takes place. The magnitude of the distributed load required to cause sudden growth of stopped elastic twins in zinc is reduced if the load is applied *before* the twins are created (which is done by means of a knife edge). This may be either because the presence of a sufficiently large distributed stress prevents the elastic twins from ever becoming stopped, or alternatively because in the alternative case (twins created first, load applied afterwards) the stopped

twin interface becomes locked in position through some kind of ageing process. There is evidence for an ageing process in twinned calcite (§ 3.3.1). The behaviour of calcite and especially of sodium nitrate approaches that of zinc when these compounds are loaded at high temperature. They then become capable of slip and almost all elastic twins are stopped; even at room temperature the spreading elastic twin in calcite meets obstacles, as witness the step-wise nature of the spread, but the obstacles are not usually powerful enough to stop the twin altogether.

3.2.6. *Twinning and Internal Friction*

Worrell and Sievert (1951) identified a peak in the relaxation spectrum of a manganese-copper alloy as being due to cyclic changes in thickness of the polysynthetic twins which they observed in the microstructure.* It is to be expected that other metals in which twinning is found will show relaxation effects of the same kind, and possibly valuable dynamic information might be obtained in this way. Internal friction peaks due to domain displacement in antiferromagnetic CoO (Fine 1952) and in magnetite (Fine 1954), are closely analogous to the effects which true twins should engender. Jones and Munro (1953) have observed elastic hysteresis and energy absorption in uranium tested in slow tension and compression, and have attributed this to mechanically induced twinning and untwinning.

*3.2.7. *Twinning and Martensitic Phase Transformations*

Martensitic transformations, so called by metallurgists in honour of Martens, the discoverer of the first transformation of this type, are diffusionless phase changes which take place by cooperative motions of large numbers of atoms. The motions rather closely resemble a pure shear, but there are small differences best described by describing the atom motions as involving two separate shears. Good reviews have been written by Bowles and Barrett (1953) and by Hall (1954). Individual lamellae are usually formed suddenly and fully fledged, to the accompaniment of a 'cry', but instances are now known of a stepwise, reversible growth of existing lamellae accompanying a stepwise increase or decrease of temperature (Kurdyumov and Khandros 1949, aluminium bronze; Chang and Read 1951, gold-cadmium alloy). This is exactly analogous to elastic twinning, with the role of stress being taken by temperature. The present writer has proposed (1953 c) that *thermoelastic* martensitic transformations of this kind may be the consequence of an exceptionally small change of density on transformation, which would reduce the internal stresses set up at the lamella interfaces.

Direct mechanical stress is known to affect martensitic transformations. Even a purely elastic stress may do so, as was discovered by Reynolds and Bever (1952). Metastable beta brass partly transforms by a martensitic process when loaded, and the plates disappear when the load is taken off.

* Basinski and Christian (1951) have since shown that these 'twins' are in fact martensitic plates; these can cause internal friction, like twins.

Faint traces of the plates remain, however, and renewed loading causes plates to grow in the same places as before (cf. similar behaviour of calcite, above). Titanium-manganese alloy behaves rather similarly (A. J. Williams, private communication).

Basinski and Christian (1954 a) and Burkart and Read (1953) independently discovered what they termed rubber-like elasticity in crystals of an alloy of indium and thallium which had been twinned in the course of martensitic transformation. (The origin of this twinning has been explained by Basinski and Christian 1954 b.) These crystals contained a single family of lamellae, and when a crystal was bent at room temperature, it behaved plastically. The twin lamellae changed in thickness as the crystal changed shape, and when the stress was released the crystal maintained its new shape. A similar test carried out in liquid air however resulted in the crystal springing back to its original shape; the twin lamellae of course resumed their original thickness. The nature of the action at a distance, which is able to recall a twin interface to its original position after that interface has moved through a distance which is very large on an atomic scale, is as yet entirely obscure. Similar rubber-like behaviour has been recorded in a gold-cadmium alloy (Chang and Read 1951). (Compare the behaviour of Rochelle salt, § 3.2.3.) Both the indium-thallium alloy and the gold-cadmium alloy behave in a thermo-elastic fashion during the martensitic transformation, and in both the growth of martensite lamellae can be retarded by *thermal stabilization*; i.e., if the slow continuous cooling which normally causes a slow growth of the lamellae, is interrupted for a while, the lamellae will not resume growth until the temperature has been lowered a finite amount. This should be compared with the ageing effect in calcite *twins* described in the following section.

Yet another analogy between twinning and martensitic transformation is the existence (unusual it is true) of isothermal transformation, taking place in irregular bursts, in certain steels (Kurdyumov and Maksimova 1948, 1950, Machlin and Cohen 1952). This is the analogue of delayed twinning, as observed in zinc and cadmium (Thompson and Millard 1952).

The purpose of the comparisons made in this section is to emphasize that discoveries in the one field may be of assistance to research in the other, because twinning and martensitic transformations are crystallographically so similar.

3.3. *Experimental Facts—The Annealing of Twins*

*3.3.1. *Ageing Effects*

Garber (1946) discovered that the resistance of residual (parallel-sided) twin lamellae in calcite against change in thickness could be greatly increased by annealing the specimen at 400–550°C. In an untreated crystal the same value of applied stress was required to make a lamella thicker or thinner, according to a sign of stress. This was still true after annealing, but the necessary stress was anything up to five times

larger; usually the ratio was near two. If a *new* twin was created in an already twinned crystal which had been heat-treated, the resistance to change of thickness of the new twin was only as great as that of the original twin *before* heat treatment. Garber concluded that the annealing affected the twin interface and not the crystal as a whole. The nature of the effect is not known, but it may well be due to a congregation of impurity atoms at the interface, which would restrain its motion. This would be analogous to the restraint of isolated dislocations in iron by atoms of nitrogen or carbon, now a well-established effect (Cottrell and Bilby 1949).

There are indications of a similar effect in zinc (Bell, private communication) and the thermal stabilization of the phase transformation in certain alloys *may* be a related phenomenon; but the necessity of postulating interaction at a large distance between dislocations and impurities raises doubts about this explanation (cf. 3.2.7).

*3.3.2. *Disappearance or Swelling of Twins as a Result of Annealing*

When a crystal containing twin lamellae is annealed, any or all of three distinct things can happen:

- (i) The lamellae may contract, so that the sharp edges of the 'lens' become blunted, and eventually may disappear entirely;
- (ii) the lamellae may balloon out at an edge, giving rise to a large grain having the same orientation as the lamella; or
- (iii) the specimen may recrystallize, in the metallurgical sense, i.e. new grains are nucleated and grow at the expense of the lamellae and the crystal immediately adjoining the lamellae. Such grains have orientations which were not present before.

(i) *Contraction*.—This has been observed in iron, pure or containing silicon or nickel (Krivobok 1926, Dunn 1946, Garber, Gindin *et al.* 1950, Cahn, Brown and Clare, unpublished work on meteorite); in zinc (Mathewson and Phillips 1927) bismuth (Gindin and Startsev 1950), calcite and sodium nitrate (Garber 1947 b). From the published results the following generalizations can be made. Long anneals at high temperature are needed to have any appreciable effect. Only thin twins are absorbed; in iron, only those about 10 microns or less in thickness, for zinc and beryllium rather thicker twins can also be absorbed. Lens-shaped twins are always absorbed from the edges; the thin, almost parallel-sided twins, in iron or sodium nitrate, are usually punctured in several places and each piece contracts independently. Absorption is always very gradual, and no sudden cooperative jumps have ever been observed. When a twin has disappeared, there may still be a faint ghost remaining visible (Dunn 1946); it has not been determined whether renewed stressing would reproduce a twin at the site of such a ghost. In uranium it was observed that lens-shaped twins of the second kind (i.e. with irrational K_1 plane) became strictly parallel-sided, like

annealing twins; also two lamellae close together might partly merge to give an H-shaped formation, a configuration which is characteristic of annealing twins. In calcite and sodium nitrate it was also noted that thin layers of crystal in the original orientation might be absorbed by the confining twin lamellae and adopt the orientation of the latter.

A peculiar feature of mechanical twins in iron and in chromium (Carrington 1953) is the serrated aspect of the lamellae. Under high magnification the lamellae are seen to be interrupted by V-shaped nicks which often are so deep as almost to sever them. Nothing of this kind is known in other substances. Since the shear across a lamella is proportional to the twin thickness, the strain gradients at such nicks must be very great. Presumably absorption of the lamellae or annealing starts at these nicks, but this has not been proved.

(ii) *Growth*.—The expansion of a twin lamella into a larger grain of identical orientation is distinctly unusual. Pfeil (1926, 1927) and Krivobok (1926) have occasionally observed this to happen in pure iron; Pfeil's observations suggest that iron which had undergone some slip as well as twinning was particularly liable to behave in this way. Bent zinc crystals (Mathewson and Phillips 1927), and uranium (Cahn 1953 a) sometimes did the same.

*3.3.3. *Recrystallization*

Metal which has been deformed by slip and twinning simultaneously will always recrystallize first where the twin lamellae are. Indeed metals such as zinc which have only one slip plane, and whose structure is not much disturbed by slip, will not recrystallize at all unless some twins are present (Kuznetsov and Zolotov 1934, 1935). When twins are present, heating to a sufficiently high temperature will lead, after an induction period, to the appearance of new grains, which do not grow far past the twinned portion. Grains appeared most quickly where lamellae impinged on each other (Kuznetsov and Karpova 1935, Jillson 1950, Bruckner 1954) but isolated twins, especially if thick, could also sometimes give rise to new grains. Little is known about the orientation of the new grains. Zolotov (1943) on the basis of a somewhat unsatisfactory experiment with zinc, concluded that all the new grains had orientations differing by only a few degrees from the orientation of the family of twin lamellae from which they grew. Experiments by the present writer have suggested that the extensive accommodation slip accompanying intense twinning may be the important source of recrystallization nuclei. The system of thousands of tiny *impinging* twins under a scratch on a zinc cleavage surface partly recrystallizes at the instant of scratching, while large twins such as those produced by cleavage or by the impact of a needle remain unaffected even after prolonged annealing. If the thin recrystallized layer was electropolished away from the scratched zinc crystals, the remaining more thinly distributed twin lamellae under the scratch were all absorbed on further annealing and little recrystallization was

observed. These observations suggest that the nuclei of the new grains are formed where twins are densely arrayed, at the instant of twinning and the subsequent heating merely causes the grains to grow.

3.4. *Piezocrescence*

Dauphiné twinning in quartz was referred to earlier (§ 1.1.2) in connection with the α - β phase-change in quartz. The atomic positions in the two individuals of a Dauphiné twin (twin axis= $[0001]$, 180° rotation) are sketched in fig. 5. The interface in this figure has been drawn straight and parallel to a diad axis, and indeed this configuration is occasionally observed (Wooster *et al.* 1947, Perez 1952); more usually, however, the interface is irregular in form.

Zinserling (1941) was the first to discover that a Dauphiné twin interface could be made to move by applying pressure, and Frondel (1945) has confirmed this. Zinserling and Shubnikov (1933) had also observed that a blow with a sharp point on a crystal face of an untwinned quartz crystal produced a symmetrical pattern of twinned material near the point of impact. The shape of the pattern depended on the crystal face chosen.

Wooster and co-workers (1947) studied the stress-induced migration of existing twin interfaces in quartz in more detail, and a full account, including a theoretical interpretation of the observations, was published by Thomas and Wooster (1951). They introduced the term *piezocrescence*, which means 'growth under pressure'. Migration could be induced by suitably distributed stress, which has to be inhomogeneous. Torque gave the best results. One individual could often be made to disappear altogether (which was the practical purpose of the investigation). The direction of motion of an interface was unaffected by a complete reversal of the signs of the applied stresses; this is the most unusual part of the results. Migration rates were appreciable only at temperature approaching the transformation point, and a temperature gradient generated sufficient stress to move an interface.

Correlation of the orientation of each specimen with the stress system empirically observed to cause untwinning firmly established that the interface always moves in such a way as to diminish the elastic energy of the system. Quartz is elastically inhomogeneous, and if by untwinning the orientation of the previously twinned part of the specimen becomes stiffer with respect to the applied stress, the elastic energy is diminished. This is true irrespective of the sign of the stress. The rule is a corollary of le Chatelier's Principle. The impact patterns observed by Shubnikov and Zinserling are determined by the same rule.

Pérez (1952) made similar observations independently, twisting twinned specimens at 480°C . By taking piezoelectric measurements during the treatment he was able to show that when the interface moved it did so in very rapid jerks (from one impurity barrier to the next?).

He obtained some evidence showing that the exact shape of the interface was determined by considerations of surface energy.

Piezocrescence differs from ordinary mechanical twinning in two respects :—(a) There is no macroscopic change of shape of the specimen, beyond the minute change of elastic strain caused by the alteration of elastic stiffness as the interface migrates. (b) The sense of migration of the interface is independent of the sign of the stress. The first fact shows that there is no question of homogeneous shear here. The small atomic shifts accompanying interface migration have zero macroscopic resultant. The best comparison is with the atomic shifts involved in recrystallization, when the boundary of a growing grain traverses the specimen. Wooster believes that the smallness of the atomic shift is essential for piezocrescence. If the shifts were not small, Si-O bonds would be ruptured, which could hardly be achieved by mechanical force alone.

Chernysheva's (1950) observations on the thickening of twin lamellae in Rochelle salt round the point of contact of a sphere pressed into a crystal are superficially similar to Zinserling and Shubnikov's, in that a similar symmetrical pattern of areas is found; in some areas the one orientation grows at the expense of the second, in the other areas the second orientation grows. These areas, however, contain families of ordinary shear twins. True piezocrescence cannot be explained by postulating the presence of submicroscopically thin lamellar twins in quartz, because of the observed independence of the effects of the sign of the stress.

3.5. *Theory of Mechanical Twinning*

The primary purpose of the present review is to collect known facts and well substantiated generalizations. The theory of mechanical twinning is as yet in a rudimentary state, and mostly of a speculative nature. In this section therefore it will be sufficient to refer briefly to the principal ideas which have been put forward and to point out the problems which are still unsolved.

*3.5.1. *Theory of Elastic Twinning*

Lifshits and Obreimov (1948) have developed a semi-quantitative theory of elastic twinning in considerable detail. A number of approximations are necessarily involved. The most important of these is the assumed force-displacement relationship for neighbouring atoms. When the lattice is sheared, the force between neighbouring atoms is assumed to increase linearly with the displacement until half the twinning shear is achieved. Then the sign of the stress is assumed suddenly to be reversed while the stress magnitude remains constant; further shear proceeds under falling stress till the twinned position is reached. There is thus a discontinuity in the relationship. A point-load is applied at the surface of a crystal and its effect on the atoms below the point of application is calculated on the basis of the idealized elastic properties of the lattice. The stage of discontinuity is eventually reached at the atoms just below

the loading point and a monoatomic twinned layer is formed. The twinned atoms now exert a supplementary force on the untwinned atoms near them, so that increase of the load will cause the twin to spread beyond the region of the loading point. The tip of the twinned layer has now taken over the stress-concentrating function of the point-load. The theory is able to account for the existence of an elastic limit, for the hysteresis on the unloading cycle, and for the eventual instability of an elastic twin which causes it to spread instantaneously across the crystal. The theory is not sufficiently quantitative to permit calculation of the expected form of the relationship between load and twin size, and in particular it does not account for the steps in this relationship. Nevertheless the theory represents a remarkable effort of calculation. A more detailed résumé is given elsewhere (Cahn 1953 c).

Lifshits (1950) has supplemented this theory with a purely macroscopic treatment of the stresses and strains near a wedge-shaped elastic twin lamella. The most interesting conclusion is that there is a limiting wedge angle for such a lamella; if this is exceeded, the stresses at the interface become locally infinite. This limiting angle is inversely proportional to the magnitude of shear, which is identical with the present writer's postulate mentioned earlier (§3.1.6). The existence of a limiting wedge angle θ accounts for the inability of twin lamellae to spread through a crystal containing a substructure of mutually tilted blocks (cf. §3.2.4) if the angle of tilt exceeds 2θ . This is because, as Lifshits shows, any sudden change of slope of the interface also leads to discontinuous stresses and there is a limit of 2θ to the possible smooth change of slope.

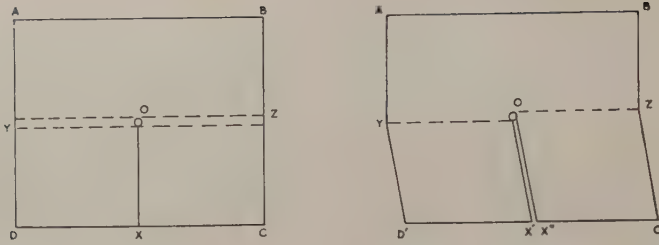
These theories do not take into account the possibility of accommodation bending (§3.1.6). Presumably the tip of a twin is tied down by the bend plane which meets it and this prevents elastic behaviour of metallic twin lamellae. Dislocations and their associated stress systems are not brought into the theory either, though the macroscopic configuration of a twin lamella would certainly be affected by their presence. A preliminary calculation of the most stable shape of a lens-shaped twin nucleus containing dislocations at the surface (see next section) has been made by Orowan (1954), and he concludes that the radius of the lens should be about twelve times its thickness in zinc.

The absence of elastic twinning in metals has been attributed to interference by slip associated with a spreading twin lamella. This interpretation is confirmed by the observations that twins cease to behave elastically in non-metals when slip or local fracture become serious. The experiments of Mügge (1888) on barium chloride (§3.1.6.1) and of Chernysheva (1950) and Fischer (1954) on Rochelle salt, among others, have established this.

3.5.2. Dislocation Theory of Twinning

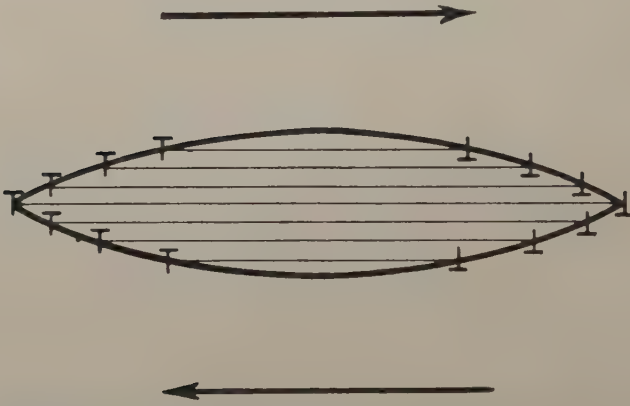
There are two distinct reasons for believing that dislocations play an essential part in the formation and development of a mechanical twin lamella. Firstly, the stress needed to make an existing lamella thicken

Fig. 26



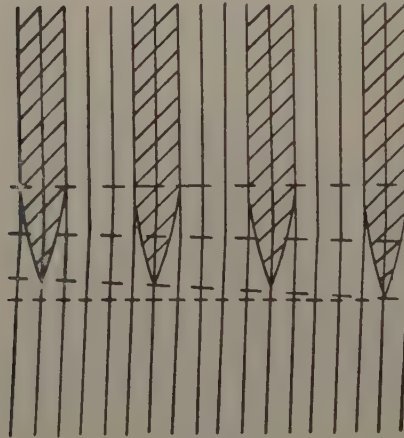
A twinning dislocation at a step in the twin interface in cadmium.
(From Thompson and Millard 1952.)

Fig. 27



Position of twinning dislocations on a lens-shaped twin lamella.
(After Orowan 1954.)

Fig. 28



Lattice bending associated with a terminating array of twin lamellae.
(After Basinski and Christian 1954.)

falls short by a large factor of the theoretical stress. (This may not be so at the stage of twin nucleation, when concentrated stresses of unknown magnitude are operating.) Since the shear of adjacent lattice planes is smaller than in slip, the discrepancy is smaller for twinning than for slip, and Orowan (1954), on the basis of semi-quantitative calculations, believes that twinning dislocations may be spontaneously generated in pairs under the influence of stress concentrations such as might be found in practice. Once the dislocations are there, their motion will cause a twin to thicken under much smaller stress than would be needed in their absence; the arguments here are just the same as in the case of slip.

Secondly, the existence of lens-shaped twins implies the presence of twinning dislocations as a simple geometrical corollary. The amount of shear across a lamella is proportional to its thickness, and where the thickness changes by one lattice parameter the amount of shear changes discontinuously by a small amount. This discontinuous change is provided by a *twinning dislocation* situated at the step. Figure 26, taken from a paper by Thompson and Millard (1952), illustrates a twinning dislocation in cadmium. It will be noticed that the number of lattice planes seen in cross section above and below the twin interface differ by one; this is a characteristic of dislocations.

In slip, the dislocations and therefore the shear displacement are concentrated in a few individual planes only, but in twinning each individual plane must undergo the same amount of shear. In slip, the concentration of slip in a few planes is nowadays attributed to the existence of dislocation *sources* each of which can generate many dislocations all in the same plane. In twinning, the same mechanism is postulated, but with a difference which ensures that each successive dislocation generated by the source appears in the lattice plane adjacent to the plane containing the previous one. For the details of this mechanism, independently introduced by Cottrell and Bilby (1952) and by Thompson and Millard (1952), the reader is referred to these papers or to the exposition by Hall (1954). Bilby (1953) has reached the general conclusion that a suitable dislocation mechanism is always available in any crystal, but that in general a nucleus of the twin orientation, several parameters in thickness, must be present before the mechanism can operate. The body-centred metals, such as iron, are an exception in this respect. As a twin develops, a closed dislocation loop is generated on each successive plane and proceeds to spread in that plane. Unless the lamella spreads right across the crystal, the dislocations become immobilized in a pattern as sketched in fig. 27, and the result is a lens-shaped twin.

Lifshits and Obreimov's theory of elastic twinning makes no overt reference to dislocations, but the concept appears to be implicit in their treatment. However, in elastic twinning as pictured by these authors there is no provision for the passage of a dislocation from plane to plane; indeed there is no dislocation source. A separate dislocation has to be created at the free surface on each successive plane of the lamella and

must then travel into the interior of the crystal: in other words, dislocations must be *created*. This is what Orowan (1954) explicitly postulates; he argues that quite moderate stress concentrations should suffice to do this, since the discrepancy between estimated theoretical and observed twinning stresses is much smaller for twinning than it is for slip. The nature of the passage from this stage to the stage at which thick residual twins are formed, presumably by the source mechanism, is not at all clear.

The necessity for a stress concentration to initiate the development of a twin lamella is now generally recognized by the theorists. The most precise picture to date of the nature of this concentration has been provided by Bilby and Entwisle (1954). Basing themselves on certain observations in the literature on the relationship between active slip planes and active twin planes, they postulate that piled-up slip dislocations generate a high local stress on one or more of the twinning planes, large enough to trigger the nucleation of twin lamellae. In particular, this may happen at a bend plane (sub-boundary), which is in line with the observation by Burke and Hibbard (1952), that twins in magnesium often spread from a bend plane. Bilby and Entwisle's calculations show that that twin plane should operate on which the resolved shear stress in the twinning direction is a maximum, as is indeed observed (§ 3.2.1). This is however merely coincidental on their model—the physically significant stress is that resolved on the active slip plane, which is responsible for piling up the slip dislocations. It will be difficult to devise a critical experiment to decide between this theory and theories in which the resolved stress in the twin plane is directly the determining factor.

3.5.3. *Theory of Annealing Effects*

The temperature-induced absorption of a twin lamella by the enveloping crystal is theoretically very difficult to understand. In a lens-shaped lamella the associated strain discontinuities are distributed over the whole of the curved interface. When the lamella is blunted under the influence of annealing, relative shear of the opposite sides of the lamella changes brusquely from a large value near the blunted tip, to zero just ahead of it. The situation here is quite different from that in, say, the experiment of Dunn, Daniels and Bolton (1950), in which a pair of twin-related crystals made by growth assume the interface of lowest energy, because in that experiment no mechanical shear was involved.

At first sight the theoretical difficulty can be overcome by dislocation theory. In a blunted twin lamella the twinning dislocations, which before were distributed over the curved twin interface, are arrayed in a wall approximately normal to the twinning direction. This is precisely what happens in the *polygonization* of crystals plastically bent by slip (Cottrell 1949). There is however an important difference. In a polygonized bent crystal each dislocation wall passes right through the crystal, or else meets two other walls. In the blunted twin lamella the short wall ends abruptly inside the crystal. A process akin to polygonization does exist in twinned crystals. Basinski and Christian

(1954 b) showed theoretically that if a crystal contains an array of parallel twinned lamellae which all taper away as sketched in fig. 28, there is a small bend at the diffuse 'interface' between the twinned and untwinned regions. The angle of tilt depends on the twinning shear and on the thickness of the twin lamellae. This configuration is energetically favourable, just as the corresponding configuration is in a polygonized slipped crystal, and moreover just such bends have been observed in indium-thallium alloys, twinned as a result of phase transformation (Basinski and Christian 1954 a). Bends associated with such twin configurations have also been found in barium titanate by Forsbergh (1949). In both cases the array of parallel twin lamella extended right across the crystal, and there was no evidence of any tendency for the lamella to become blunted, though the specimens had been at high temperature. When a single lamella becomes blunted, there is a local small-angle bend opposite the blunted end, but no bend either side of the twin.

Twin blunting has only been observed when the lamella is thin. This suggests that there is some factor energetically favourable to blunting which counteracts the increase of elastic energy which at first sight is the sole consequence of blunting. This increase of energy would be expected to be greater for thicker twins. The nature of the counter-acting factor remains to be discovered; it may simply be the associated decrease in the total volume of twinned, and therefore strained material.

Similar energetic difficulties arise in interpreting the swelling of twin lamellae on annealing. Once the swelling is well under way there is no difficulty in understanding why it should continue, but the first stages appear to be associated with an increase of elastic energy. Before too much trouble is taken in attempting to explain this phenomenon it would be advisable to have further and more detailed experimental data.

The ready recrystallization at the site of twin lamellae and especially at their intersections is in line with the body of experimental evidence which shows that new grains are nucleated at points of high internal strain. The as yet somewhat uncertain observations on the approximate similarity between the orientations of the twin lamellae and of the new grains, if properly confirmed, promise to be of considerable theoretical interest, because they suggest that the new grains have grown from fragments of the twin lamellae which have first become strain-free by a mechanism such as that suggested by Cahn (1950) or that put forward by Orowan (1954). Direct evidence for such a mechanism would in turn have a bearing on the genesis of recrystallization textures.

ACKNOWLEDGMENTS

Professor J. D. H. Donnay provided much useful advice and information towards the writing of this review. Thanks are also due to Professor F. Laves, Dr. D. T. Griggs, Mr. R. L. Bell, and Mr. A. J. Williams, for providing information about their experiments before publication.

Professor Laves kindly provided two illustrations. Several publishers kindly consented to the reproduction of illustrations; acknowledgements to individual publishers are made in the captions.

REFERENCES

- AMINOFF, G., and BROOMÉ, G., 1931, *Z. Krist.*, **80**, 355.
 ANCKER, B., 1953, *Ann. Physik, Ser. 12*, **6**, 121, 145.
 ANSEL, G., 1948, *Metals Handbook*, p. 975 (Cleveland: Amer. Soc. Metals).
 ARMSTRONG, E., 1946, *American Mineralogist*, **31**, 456.
 AUST, K. T., KRILL, F. M., and MORRAL, F. R., 1952, *Trans. Amer. Inst. Min. Metall. Engrs.*, **194**, 865.
 BAKARIAN, P. W., and MATHEWSON, C. H., 1943, *Trans. Amer. Inst. Min. Metall. Engrs.*, **152**, 226.
 BARNES, R. S., 1950, *Nature, Lond.*, **166**, 1032.
 BARRETT, C. S., 1945, *Trans. Amer. Inst. Min. Metall. Engrs.*, **161**, 15; 1948, *Cold Working of Metals* (Cleveland: Amer. Soc. Metals); 1950, *Trans. Amer. Inst. Min. Metall. Engrs.*, **188**, 123; 1952, *Structure of Metals* (New York: McGraw-Hill).
 BARRETT, C. S., ANSEL, G., and MEHL, R. F., 1937, *Trans. Amer. Soc. Metals*, **25**, 702.
 BARRETT, C. S., and HALLER, C. T., 1947, *Trans. Amer. Inst. Min. Metall. Engrs.*, **171**, 246.
 BASINSKI, Z. S., and CHRISTIAN, J. W., 1951, *J. Inst. Metals*, **80**, 659; 1954 a, *Acta Metallurgica*, **2**, 101; 1954 b, *Ibid.*, **2**, 148.
 BAUMHAUER, H., 1911, *Z. Krist.*, **49**, 118.
 BECHTOLD, J. H., 1953, *Trans. Amer. Inst. Min. Metall. Engrs.*, **197**, 1469.
 BELL, R. L., and CAHN, R. W., 1953, *Acta Metallurgica*, **1**, 752.
 BERG, W. F., 1934, *Nature, Lond.*, **134**, 143.
 BILBY, B. A., 1951, *Phil. Mag.*, **44**, 782; 1953, *Year Book of the Roy. Soc.*, p. 218.
 BILBY, B. A., and BULLOUGH, R., 1954, *Phil. Mag.*, **45**, 631.
 BILBY, B. A., and ENTWISLE, A. R., 1954, *Acta Metallurgica*, **2**, 15.
 BIRINGUCCIO, V., 1540, *Pirotechnia* (Venice: Navo).
 BOAS, W., and HONEYCOMBE, R. W. K., 1946, *Proc. Roy. Soc. A*, **186**, 57.
 BOND, W. L., and ANDRUS, J., *American Mineralogist*, **37**, 622.
 BOWLES, J. S., and BARRETT, C. S., 1953, *Progress in Metal Physics*, Vol. 3 (London: Pergamon Press).
 BOWLES, J. S., and MACKENZIE, J. K., 1954, *Acta Metallurgica*, **2**, 129, 138.
 BRAGG, W. L., 1937, *The Atomic Structure of Minerals* (Ithaca: Cornell University Press).
 BRASSEUR, H., and RASSENFOSSE, A. DE, 1941, *Mem. Soc. Roy. Sci. Liege*, **4**, 397.
 BĚEZINA, A., 1880, *Verh. Geol. Reichsanstalt Wien*, p. 45.
 BRILLIANTOV, N. A., and OBREIMOV, I. V., 1935, *Zh. Eksper. Teoret. Fiz.*, **5**, 330; 1937, *Ibid.*, **7**, 978.
 BRILLIANTOV, N. A., and STARTSEV, V. I., 1939, *Zh. Eksper. Teoret. Fiz.*, **9**, 532.
 BRUCKNER, H. M., 1954, *Acta Metallurgica*, **2**, 168.
 BUCKLEY, H. E., 1951, *Crystal Growth* (New York: Wiley).
 BUERGER, M. J., 1945, *American Mineralogist*, **30**, 469; 1951, in *Phase Transformations in Solids* (ed. R. Smoluchowski), p. 183 (New York: Wiley).
 BURGERS, W. G., 1946, *Nature, Lond.*, **157**, 76.
 BURGERS, W. G., MEIJS, J. C., and TIEDEMA, T. J., 1953, *Acta Metallurgica*, **1**, 93.

- BURKART, M. W., and READ, T. A., 1953, *Trans. Amer. Inst. Min. Metall. Engrs.*, **197**, 1516.
- BURKE, E. C., and HIBBARD, W. R., 1952, *Trans. Amer. Inst. Min. Metall. Engrs.*, **194**, 295.
- BURKE, J. E., 1950, *Trans. Amer. Inst. Min. Metall. Engrs.*, **188**, 1324.
- BURKE, J. E., and BARRETT, C. S., 1948, *Trans. Amer. Inst. Min. Metall. Engrs.*, **175**, 106.
- BURKE, J. E., and TURNBULL, D., 1953, *Progress in Metal Physics*, Vol. 3, (London: Pergamon Press), p. 220.
- CAHN, R. W., 1950, *Proc. Phys. Soc. B*, **63**, 323; 1951, *Trans. Amer. Inst. Min. Metall. Engrs.*, **191**, 542; 1952, *J. Inst. Metals*, **80**, 723; 1953 a, *Acta Metallurgica*, **1**, 49; 1953 b, *Ibid.*, **1**, 176; 1953, c, *Il Nuovo Cimento (Supplemento)*, **10**, 350.
- CALNAN, E. A., and CLEWS, C. J. B., 1950, *Phil. Mag.*, **41**, 1085; 1951, *Ibid.*, **42**, 616, 919; 1952, *Ibid.*, **43**, 93.
- CARRINGTON, W. E., 1953, *J. Inst. Metals*, **82**, 170.
- CHALMERS, B., 1940, *Proc. Roy. Soc. A*, **175**, 100; 1949, *Progress in Metal Physics*, Vol. 1 (London: Butterworths Scientific Publications).
- CHALMERS, B., KING, R., and SHUTTLEWORTH, R., 1948, *Proc. Roy. Soc. A*, **193**, 465.
- CHANG, L. C., and READ, T. A., 1951, *Trans. Amer. Inst. Min. Metall. Engrs.*, **189**, 47.
- CHAUDRON, G., LACOMBE, P., and YANNAQUIS, N., 1948, *C.R. Acad. Sci. Paris*, **226**, 1372.
- CHEN, N. K., and MADDIN, R., 1951, *Trans. Amer. Inst. Min. Metall. Engrs.*, **191**, 937.
- CHERNYSHEVA, M. A., 1950, *Doklady Akad. Nauk (U.S.S.R.)*, **74**, 247.
- CHUDOBA, K. F., and FRECHEN, J., 1950, *Neues Jb. Mineralogie, Abhandl.*, **81**, 183.
- CLARK, R., and CRAIG, G. B., 1953, *Progress in Metal Physics*, Vol. 3 (London: Pergamon Press), p. 115.
- CONARD, G. P., AVERBACH, B. L., and COHEN, M., 1953, *Trans. Amer. Inst. Min. Metall. Engrs.*, **197**, 1036.
- COTTRELL, A. H., 1949, in *Progress in Metal Physics*, Vol. 1 (London: Butterworths Scientific Publications), p. 92.
- COTTRELL, A. H., and BILBY, A. H., 1949, *Proc. Phys. Soc. A*, **62**, 49; 1951, *Phil. Mag.*, **42**, 573.
- DALITZ, V. C., and BURGERS, W. G., 1949, *Verh. Kon. Akad. Wet. Amsterdam*, **52**, 627.
- DANA, E. S., and FORD, W. E., 1932, *Textbook of Mineralogy* (New York: Wiley).
- DAVIDENKOV, N. N., KOLESNIKOV, A. F., and FEDOROV, K. N., 1933, *Zh. Eksper. Teoret. Fiz.*, **3**, 350.
- DE L'ISLE, ROMÉ, 1783, *Essai de Cristallographie*.
- DEICHA, G., 1946, *C.R. Acad. Sci. Paris*, **223**, 1155; 1948, *Experientia*, **4**, 67; 1949, *Bull. Soc. Franç. Minéralogie*, **72**, 286.
- DERUYTTÈRE, A., and GREENOUGH, G. B., 1954, *Phil. Mag.*, **45**, 624.
- DONNAY, J. D. H., 1940, *American Mineralogist*, **25**, 578; 1954, Article on *Twinning*, *Encyclopaedia Britannica* (to be published).
- DONNAY, J. D. H., and DONNAY, G., 1954, Article on *Crystal Geometry*, *International Tables for X-ray Crystallography*, Vol. 2 (to be published).
- DRUGMAN, J., 1928, *Bull. Soc. Franç. Minéralogie*, **51**, 187.
- DUNN, C. G., 1946, *Trans. Amer. Inst. Min. Metall. Engrs.*, **167**, 373.
- DUNN, C. G., DANIELS, F. W., and BOLTON, M. J., 1950, *Trans. Amer. Inst. Min. Metall. Engrs.*, **188**, 368.

- EDWARDS, O. S., and LIPSON, H., 1943, *J. Inst. Metals*, **69**, 177.
- ELAM, C. F., 1928, *Proc. Roy. Soc. A*, **121**, 247.
- ELLEMAN, A. J., and WILMAN, H., 1948, *Proc. Phys. Soc.* **61**, 164; 1949, *Ibid.*, **62**, 344.
- ELLIS, W. C., 1950, *Trans. Amer. Inst. Min. Metall. Engrs.*, **188**, 886.
- ELLIS, W. C., and FAGEANT, J., 1954, *Trans. Amer. Inst. Min. Metall. Engrs.*, **200**, 291.
- ELLIS, W. C., and TREUTING, R. G., 1951, *Trans. Amer. Inst. Min. Metall. Engrs.*, **191**, 53.
- FAIRBAIRN, H. W., and HAWKES, H. E., 1941, *Amer. J. Sci.*, **239**, 617.
- FENSHAM, P. J., 1950, *J. Sci. Research Austral.*, **3**, 103, 105.
- FINE, M. E., 1952, *Phys. Rev.*, **87**, 1143.
- FINE, M. E., and KENNEY, N. T., 1954, *Phys. Rev.*, **94**, 1573.
- FISCHER, E., 1954, *Naturwiss.*, **41**, 117.
- FORSBERGH, P. W., 1949, *Phys. Rev.*, **76**, 1187.
- FÖRSTER, F., and SCHEIL, E., 1940, *Z. Metallkde.*, **32**, 165.
- FRANK, F. C., 1949, *Discussions on Crystal Growth* (London: Faraday Society), p. 67.
- FRIEDEL, G., 1904, *Études sur les Groupements Cristallins*, *Bull. Soc. Industrie Minérale*, **3**, 877; 1905, *Ibid.*, **4**, 127; 1922, *Bull. Soc. Franç. Minéralogie*, **45**, 8; 1926, *Leçons de Cristallographie* (Paris: Berger-Levrault); 1933, *Bull. Soc. Franç. Minéralogie*, **56**, 262.
- FRONDEL, C., 1945, *American Mineralogist*, **30**, 447.
- FULLMAN, R. L., 1950 a, *J. Appl. Physics*, **21**, 1049; 1950 b, *General Electric Report*, RL-422; 1951, *J. Appl. Physics*, **22**, 448, 456.
- FULLMAN, R. L., and FISHER, J. C., 1951, *J. Appl. Physics*, **22**, 1350.
- GALLAGHER, C. J., 1952, *Phys. Rev.*, **88**, 721.
- GARBER, R. I., 1938, *C.R. Acad. Sci. U.S.S.R.*, **21**, 229; 1940 a, *J. Phys. U.S.S.R.*, **2**, 313, 319; 1940 b, *Ibid.*, **3**, 179; 1946, *Zh. Eksper. Teoret. Fiz.*, **16**, 923; 1947 a, *J. Phys. U.S.S.R.*, **17**, 55; 1947 b, *Zh. Eksper. Teoret. Fiz.*, **17**, 63; 1947 c, *Dokl. Akad. Nauk (U.S.S.R.)*, **57**, 555.
- GARBER, R. I., GINDIN, I. A., KONSTANTINOVSKY, M. G., and STARTSEV, V. I., 1950, *Dokl. Akad. Nauk (U.S.S.R.)*, **74**, 343.
- GARBER, R. I., ZALIVADNY, S. YA., and STARTSEV, V. I., 1947, *Dokl. Akad. Nauk (U.S.S.R.)*, **58**, 571.
- GAUBERT, P., 1896, *Bull. Soc. Franç. Minéralogie*, **19**, 431.
- GEIL, G. W., and CARWILE, N. L., 1953, *Welding J.*, **32**, 273-S.
- GILMAN, J. J., and READ, T. A., 1952, *Trans. Amer. Inst. Min. Metall. Engrs.*, **194**, 875.
- GINDIN, I. A., and STARTSEV, V. I., 1950, *Zh. Eksper. Teoret. Fiz.*, **20**, 738.
- GOLDSCHMIDT, V., 1902, *Neues Jb. Mineralogie, Beilageband*, **15**, 562.
- GOLDSCHMIDT, V., and MÜLLER, K., 1934, *Neues Jb. Mineralogie*, **68** (A), 195.
- GRIGGS, D. T., 1938, *American Mineralogist*, **23**, 28.
- GRIGGS, D. T., and MILLER, W. B., 1951, *Bull. Geol. Soc. America*, **62**, 853.
- GRIGGS, D. T., TURNER, F. J., BORG, I., and SOSOKA, J., 1951, *Bull. Geol. Soc. America*, **62**, 1385; 1953, *Ibid.*, **64**, 1327.
- GRÜHN, A., and JOHNSEN, A., 1917 a, *Zentralblatt Mineralogie*, 366; 1917 b, *Ibid.*, 370.
- HALL, E. O., 1953, *Acta Cryst.*, **6**, 570; 1954, *Twinning and Diffusionless Transformations in Metals* (London: Butterworths Scientific Publications).
- HANDIN, J. W., and GRIGGS, D. T., 1951, *Bull. Geol. Soc. America*, **62**, 863.
- HARKER, D., and PARKER, E. A., 1945, *Trans. Amer. Soc. Metals*, **34**, 156.
- HARTMAN, P., 1953, *Thesis* (Groningen).
- HAUSNER, H. H., and PINTO, N. P., 1951, *Trans. Amer. Soc. Metals*, **43**, 1152.
- HAÜY, R. J., 1801, *Traité de Minéralogie* (Paris).

- HEIDE, F., 1931, *Z. Krist.*, **78**, 257.
- HÉRENGUEL, J., 1948, *Revue Métall.*, **45**, 139.
- HÉRENGUEL, J., and LACOMBE, P., 1949, *C.R. Acad. Sci. Paris*, **228**, 846.
- HESS, J. B., and BARRETT, C. S., 1949, *Trans. Amer. Inst. Min. Metall. Engrs.*, **185**, 599.
- HOLDEN, J., 1952, *Phil. Mag.*, **43**, 976.
- JAGODZINSKI, H., 1949, *Acta Cryst.*, **2**, 298.
- JILLSON, D. C., 1950, *Trans. Amer. Inst. Min. Metall. Engrs.*, **188**, 1009.
- JOHNSEN, A., 1907, *Neues Jb. Mineralogie, Beilageband*, **23**, 237; 1914 a, *Jahrbuch der Radioaktivität, etc.*, **226**; 1914 b, *Neues Jb. Mineralogie, Beilageband*, **39**, 500; 1916 a, *Zentralblatt Mineralogie*, **121**; 1916 b, *Ibid.*, **385**; 1917, *Ibid.*, **433**.
- JONES, E. R. W., and MUNRO, W., 1953, *J. Mech. Physics Solids*, **1**, 182.
- KAUFFMANN, A. R., GORDON, P., and LILLIE, D. W., 1950, *Trans. Amer. Soc. Metals*, **42**, 785.
- KAY, H. F., 1948, *Acta Cryst.*, **1**, 229.
- KELLY, A., 1953, *Proc. Phys. Soc. A*, **66**, 403.
- KENNEDY, S. W., UBBELOHDE, A. R., and WOODWARD, I., 1953, *Proc. Roy. Soc. A*, **219**, 303.
- KING, R., 1952, *Nature, Lond.*, **169**, 543.
- KIRAKAWA, K., 1952, *J. Phys. Soc. Japan*, **7**, 331.
- KIRCHNER, F., and CRAMER, N., 1938, *Ann. Physik*, **33**, 138.
- KLASSEN-NEKLUDOVA, M. V., CHERNYSHEVA, M. A., and SHTERNBERG, A. A., 1948, *Dokl. Akad. Nauk (U.S.S.R.)*, **63**, 527.
- KRIVOBOK, N. V., 1926, *Amer. Inst. Min. Metall. Engrs.*, Preprint 1557-E.
- KRAFFT, J. M., SULLIVAN, A. M., and TIPPER, C. F., 1953, *Proc. Roy. Soc. A*, **221**, 114.
- KRONBERG, M. L., and WILSON, F. H., *Trans. Amer. Inst. Min. Metall. Engrs.*, **185**, 501.
- KURDYUMOV, G. V., and KHANDROS, L. G., 1949, *Dokl. Akad. Nauk (U.S.S.R.)*, **66**, 211.
- KURDYUMOV, G. V., and MAKSIMOVA, O. P., 1948, *Dokl. Akad. Nauk (U.S.S.R.)*, **63**, 83; 1950, *Ibid.*, **73**, 95.
- KUZNETSOV, V. D., and KARPOVA, M. P., 1935, *Zh. Eksper. Teoret. Fiz.*, **5**, 202.
- KUZNETSOV, V. D., and ZOLOTOV, V. A., 1934, *C.R. Acad. Sci. (U.S.S.R.)*, **2**, 13; 1935, *Zh. Eksper. Teoret. Fiz.*, **5**, 75.
- LACOMBE, P., and BERGHEZAN, A., 1949, *C.R. Acad. Sci. Paris*, **228**, 93.
- LACOMBE, P., and YANNAQUIS, N., 1947, *Métaux et Corrosion*, **22**, 35.
- LAVES, F., 1952, *Naturwiss.*, **30**, 546; 1954, *Acta Cryst.* (in the press).
- LEE, H. T., and BRICK, R. M., 1953, *O.N.R. Report, Contract* 24908.
- LEHMANN, O., 1877, *Z. Krist.*, **1**, 453; 1884, *Ibid.*, **8**, 437.
- LIFSHTS, I. M., 1948, *Zh. Eksper. Teoret. Fiz.*, **18**, 1134.
- LIFSHTS, I. M., and OBREIMOV, I. V., 1948, *Izv. Akad. Nauk. Ser. Fiz. (U.S.S.R.)*, **12**, 65.
- LISTER, R. P., 1954, *Metal Progress*, **65**, 98.
- LÖFFLER, M., 1934, *Neues Jb. Mineralogie, Beilageband*, **68** (A), 125.
- LOW, J. R., and FEUSTEL, R. G., 1953, *Acta Metallurgica*, **1**, 85.
- MACHLIN, E. S., and COHEN, M., 1952, *Trans. Amer. Inst. Min. Metall. Engrs.*, **194**, 489.
- MADAN, M., 1886, *Nature, Lond.*, **34**, 66.
- MADDIN, R., MATHEWSON, C. H., and HIBBARD, W. R., 1949, *Trans. Amer. Inst. Min. Metall. Engrs.*, **185**, 655.
- MASON, W. P., MCSKIMIN, H. J., and SHOCKLEY, W., 1948, *Phys. Rev.*, **73**, 1213.
- MATHEWSON, C. H., 1928, *Amer. Inst. Min. Metall. Engrs., Proc. Inst. Metals Div.*, **7**.

- MATHEWSON, C. H., and PHILLIPS, A. J., 1927, *Trans. Amer. Inst. Min. Metall. Engrs.*, **143**.
- MATHEWSON, C. H., and VAN HORN, K., 1930, *Amer. Inst. Min. Metall. Engrs., Inst. Metals Div.*, 59.
- MATTHIAS, B., 1951, in *Phase Transformations in Solids* (ed. R. Smoluchowski) (New York: Wiley), p. 335.
- MATTHIAS, B., and VON HIPPEL, A., 1948, *Phys. Rev.*, **73**, 1378.
- McHARGUE, C. J., and HAMMOND, J. P., 1953, *Acta Metallurgica*, **1**, 700.
- McKEEHAN, J. W., 1927, *Nature, Lond.*, **120**, 392.
- MENZER, G., 1938, *Naturwiss.*, **26**, 385.
- MERZ, W. J., 1949, *Phys. Rev.*, **76**, 1221; 1954, *Ibid.*, **95**, 690.
- MILLER, R. F., 1936, *Trans. Amer. Inst. Min. Metall. Engrs.*, **122**, 176.
- MITSUI, T., and FURUICHI, J., 1953, *Phys. Rev.*, **90**, 193.
- MOORE, A. J. W., 1952, *Proc. Phys. Soc. B*, **65**, 956.
- MÜGGE, O., 1888, *Neues Jb. Mineralogie* (1), 131; 1889, *Ibid.* (1), 145; 1894, *Ibid.* (1), 107; 1910, *Nachr. Gesell. Wiss. Göttingen*, **7**, 23; 1911, *Fortschritte Mineralogie*, **1**, 38; 1930, *Z. Krist.*, **75**, 32; 1932, *Ibid.*, **82**, 59.
- MÜGGE, O., and HEIDE, F., 1931, *Neues Jb. Mineralogie, Beilageband*, **64**, 163.
- OLIVER, D. S., 1952, *Research (London)*, **5**, 45.
- OROWAN, E., 1954, in *Dislocations in Metals* (ed. M. Cohen) (New York: Amer. Inst. Min. Metall. Engrs.), p. 116.
- PAXTON, H. W., 1953, *Acta Metallurgica*, **1**, 141.
- PÉREZ, J. P., 1952, *Ann. Physique*, **7**, 238.
- PETCH, N. J., 1953, *J. Iron Steel Inst.*, **174**, 25.
- PFEIL, L. B., 1926, *Carnegie Schol. Memoirs, Iron and Steel Inst.*, **15**, 319; 1927, *Ibid.*, **16**, 153.
- PIPER, W. W., and ROTH, W. L., 1953, *Phys. Rev.*, **92**, 503.
- PRATT, P. L., 1951, *Thesis (Cambridge)*; 1953, *Acta Metallurgica*, **1**, 692.
- PRATT, P. L., and PUGH, S. F., 1952, *J. Inst. Metals*, **80**, 653.
- PRESTON, G. D., 1927, *Nature, Lond.*, **119**, 600.
- PUMPHREY, W. I., and LYONS, J. V., 1949, *Nature, Lond.*, **163**, 960.
- RAE, H., and ROBINSON, A. E., 1954, *Proc. Roy. Soc. A*, **222**, 558.
- RAMSEY, J. A., 1951, *J. Inst. Metals*, **80**, 167.
- REYNOLDS, J. E., and BEVER, M. B., *Trans. Amer. Inst. Min. Metall. Engrs.*, **194**, 1065.
- RHODES, R. G., 1951, *Acta Cryst.*, **4**, 105; 1952, *Nature, Lond.*, **170**, 369.
- ROSE, G., 1886, *Physik. Abhandl. Kön. Akad. Wiss. Berlin*, 57.
- ROSENTHAL, D., and WOOLSEY, C. C., 1952, *Welding J.*, **31**, 475-S.
- ROSI, F. D., DUBÉ, C. A., and ALEXANDER, B. H., 1953, *Trans. Amer. Inst. Min. Metall. Engrs.*, **197**, 256.
- RYBALKO, F. P., and YAKUTOVICH, M. V., 1948, *Zh. Tekh. Fiz.*, **18**, 915.
- SALKOVITZ, E. I., and VON BATCHELDER, F., 1952, *Trans. Amer. Inst. Min. Metall. Engrs.*, **194**, 165.
- SCHMID, E., and BOAS, W., 1935, *Kristallplastizität* (Berlin: Springer).
- SEIFERT, H., 1928, *Neues Jb. Mineralogie, Beilageband (A)*, **57**, 665.
- SHARP, M., and DUNN, C. G., 1952, *Trans. Amer. Inst. Min. Metall. Engrs.*, **194**, 1344.
- SHASKOLSKY, M., and SHUBNIKOV, A., 1933, *Z. Krist.*, **85**, 1.
- SLAWSON, C. B., 1950, *American Mineralogist*, **35**, 193.
- SMITH, C. S., 1948, *Trans. Amer. Inst. Min. Metall. Engrs.*, **175**, 15.
- SMITH, S. W. J., DEE, A. A., and YOUNG, J., 1928, *Proc. Roy. Soc. A*, **121**, 477.
- STARTSEV, V. I., 1940, *J. Physics, U.S.S.R.*, **3**, 107.
- STEIJN, R. P., and BRICK, R. P., 1954, *Trans. Amer. Soc. Metals*, **46**, 1406.
- TAHVONEN, P. E., 1947, *Ann. Acad. Sci. Fenn. Ser. A*, **1**, 42.
- TAYLOR, W. H., 1933, *Z. Krist.*, **85**, 425.

- TAYLOR, W. H., DARBYSHIRE, J. A., and STRUNZ, H., 1934, *Z. Krist.*, **87**, 464.
- TEAL, G. K., SPARKS, M., and BUEHLER, E., 1952, *Proc. Inst. Radio Engrs.*, **40**, 906.
- TERTSCH, H., 1949, *Die Festigkeitserscheinungen der Kristalle* (Wien : Springer).
- THOMAS, L. A., and WOOSTER, W. A., 1951, *Proc. Roy. Soc. A*, **208**, 43.
- THOMPSON, N., and MILLARD, D. J., 1952, *Phil. Mag.*, **43**, 422.
- TIEDEMA, T. J., MAY, W., and BURGERS, W. G., 1949, *Acta Cryst.*, **2**, 151.
- TIPPER, C. F., and SULLIVAN, A. M., 1951, *Trans. Amer. Soc. Metals*, **43**, 906.
- TURNER, F. J., and CH'IH, C. S., 1951, *Bull. Geol. Soc. Amer.*, **62**, 887.
- TURNER, F. J., GRIGGS, D. T., and HEARD, H., 1954, *Bull. Geol. Soc. Amer.* (in the press).
- VERMA, A. R., 1953, *Crystal Growth and Dislocations* (London : Butterworths Scientific Publications).
- VOGEL, F. L., and BRICK, R. M., 1953, *Trans. Amer. Inst. Min. Metall. Engrs.*, **197**, 700.
- VON GLISZCYNski, S., 1948, *Neues Jb. Mineralogie, Abt. A*, **79**, 1 ; 1950, *Neues Jb. Mineralogie, Monatshefte*, 25.
- WHITWHAM, D., MOUFLARD, M., and LACOMBE, P., 1951, *Trans. Amer. Inst. Min. Metall. Engrs.*, **191**, 1070.
- WOOD, E. A., 1951, *Bell System Tech. J.*, **30**, 945.
- WOOSTER, W. A., WOOSTER, N., RYCROFT, J. L., and THOMAS, L. A., 1947, *J. Inst. Elect. Engrs.*, **94** (Part IIIA), 927.
- WORRELL, F. T., and A. V. SIEVERT, 1951, *J. Appl. Physics*, **22**, 1257.
- WYROUBOFF, M., 1886, *Bull. Soc. Franç. Minéralogie*, **9**, 262 ; 1891, *Ibid.*, **14**, 233.
- YAKOVLEVA, E. S., and YAKUTOVICH, M. V., *Zh. Eksper. Teoret. Fiz.*, **10**, 1146 ; 1950, *Zh. Tekh. Fiz.*, **20**, 420.
- YAKUTOVICH, M. V., and YAKOVLEVA, E. S., 1939, *Zh. Eksper. Teoret. Fiz.*, **9**, 882.
- ZAPFEE, C. A., 1953, *Z. Metallkde.*, **44**, 397.
- ZINSERLING, E. V., 1941, *C.R. Acad. Sci., U.S.S.R.*, **33**, 365, 368 ; 1953, *Dokl. Akad. Nauk (U.S.S.R.)*, **90**, 785.
- ZINSERLING, E. V., and SHUBNIKOV, A., 1933, *Z. Krist.*, **85**, 454.
- ZOLOTOV, V. A., 1943, *C.R. Acad. Sci. U.S.S.R.*, **39**, 180.

Electronic Structure of Primary Solid Solutions in Metals

By J. FRIEDEL

Centre de Recherches Metallurgiques de l'Ecole des Mines de Paris

CONTENTS

| | |
|--|--|
| § 1. INTRODUCTION. | |
| § 2. PERTURBED METALLIC LATTICE. GENERAL RESULTS AND APPROXIMATIONS. | |
| 2.1. Given perturbation acting on one electron. | |
| 2.1.1. Energy bands. Extended and bound states. | |
| 2.1.2. Boundary conditions. | |
| 2.1.3. Approximations used. | |
| 2.1.3.1. Perturbation method. | |
| 2.1.3.2. Insulators. | |
| 2.1.3.3. Metals. | |
| 2.2. Self consistent solution in an alloy. | |
| 2.2.1. Molecular and atomic orbitals. | |
| 2.2.2. Screening. Displacement of the Fermi level. | |
| 2.2.3. Large supplementary charges. | |
| § 3. MOLECULAR ORBITALS. FIRST ORDER APPROXIMATION. | |
| 3.1. Assumptions of the method. | |
| 3.2. Self consistent perturbation. | |
| 3.3. Range of interaction for impurities. | |
| 3.4. Delocalization of the screening. | |
| 3.5. Density of states. Rigid band structure. | |
| 3.6. Overlapping bands. Ferromagnetic alloys. | |
| 3.7. Energies of solution. Interaction between impurities. | |
| 3.7.1. Energies of solution. | |
| 3.7.2. Vacancies. | |
| 3.7.3. Exchange correction. | |
| 3.7.4. Energies of solution at large concentrations. | |
| 3.7.5. Interaction between solute atoms. | |
| 3.7.6. Displacement of the optical absorption edge in alloys. | |
| 3.8. The Born approximation. Electrical properties. | |
| 3.8.1. Relation between screening and phase shifts. | |
| 3.8.2. The Born approximation. | |
| 3.8.3. Electrical resistivity due to impurities. | |
| 3.8.4. Thermoelectric power. | |
| § 4. MOLECULAR ORBITALS. BETTER APPROXIMATIONS. | |
| 4.1. Second order approximation. | |
| 4.1.1. Charge locally displaced. Fe alloys. | |
| 4.1.2. Density of states. | |
| 4.1.3. The perturbing potential. | |
| 4.1.4. Hume-Rothery rules. | |
| 4.2. Parabolic bands. | |
| 4.2.1. The perturbing potential. | |
| 4.2.2. Density of states. | |
| 4.2.3. Phase shifts. | |
| 4.3. Full bands. | |
| § 5. ATOMIC ORBITALS. | |
| 5.1. Magnetic susceptibility of Cu Al. | |
| 5.2. Energies of dissolution. | |
| 5.3. X-rays and optical transitions in metals. | |
| 5.3.1. Fine structures. | |
| 5.3.2. Absorption coefficient at the main edge. | |
| 5.3.3. Absorption and emission edges. | |
| 5.4. Objections to atomic orbitals. | |
| 5.4.1. Hume-Rothery rules. | |
| 5.4.2. Magnetic properties. | |
| APPENDIX. THE SIZE FACTOR. | |
| REFERENCES. | |

§ 1. INTRODUCTION

THE purpose of this paper is to study the electronic structure of alloys. In principle, this is simply a question of solving a Schrodinger equation. In metallic substances however the some 10^{24} conduction electrons per unit volume must all be treated together (Sommerfeld 1928). An exact solution is impossible, and simplifications must be made: only impurities in metals will be considered, and the various factors deduced experimentally by Hume-Rothery (1931) will be treated separately.

By impurities, it is meant that a metal A contains an element B in small enough quantities for the B atoms to be dispersed in the matrix A and to interact only weakly. This applies usually to the range of *primary solid solutions* and to some other disordered phases.

The study of the phase boundaries in alloys led Hume-Rothery to separate three factors, referred to here as valence, size and polarization, which will now be described.

Valence: some phase boundaries seem to be related to special values of the average number of valence electrons per lattice site. This number is altered when interstitial atoms are introduced or atoms with different valencies substituted in the matrix.

Size: the Pauli principle prevents the inner electrons of atoms B from overlapping very much those of the matrix A. This distorts the lattice A somewhat and imposes some conditions on the size of interstitial and substitutional impurities dissolving easily in a given matrix.

Polarization: more 'electropositive' elements, i.e. those above or on the right of the matrix in the periodic table, tend to give up part of their valence electrons to the matrix, thus leading at high concentrations to stable ordered intermetallic compounds with some ionic character. At small concentrations, the charge given up by the impurity remains on the neighbouring atoms of the matrix, and the conduction band may be considered as locally polarized by the impurity. Mutual polarization of the inner shells may also possibly lead to some interaction of a van der Waals type between atoms.

These factors will be treated separately, an admittedly poor approximation when more than one factor is important. The emphasis will be on effects related to a difference of *valency* between solute and solvent, because this is the case in most alloys; polarization between elements with the same valency and size effects will be briefly considered (§ 2. Appendix) and shown to be often small.

The main problem of interest will thus be what happens to the conduction electrons of a metal when a localized charge is introduced in an interstitial or substitutional position. Difficulties arise through the lack of symmetry and the great number of particles involved.

Owing to lack of symmetry, approximate methods are necessary to study the movement of an electron in a perturbed lattice. These are

summarized in § 2, together with some general results on energy bands and bound states.

The potential acting on an electron is then computed in a self consistent way by taking some average density of the other electrons, using a Hartree or Hartree-Fock method. Correlation between electrons may be taken somewhat into account by the way the averages are made. This leads to two different approximations corresponding to the 'molecular' and 'atomic' orbitals used in chemistry. As usual, the molecular orbitals (§ 3, 4) are better suited to study fast electrons and properties related to the Fermi level: electrical properties, para- and ferromagnetism, electronic specific heat, Hume-Rothery rules, interactions between impurities, etc. . . . The atomic orbitals are perhaps more suitable to compute the energies of dissolution (§ 5).

§ 2. PERTURBED METALLIC LATTICE. GENERAL RESULTS AND APPROXIMATIONS

When a foreign atom or similar disturbance is introduced into a metal, the periodic lattice field is perturbed. The problem of the effect of this perturbation on the electron can be divided in two parts: first, the study of the quantized states of an electron in a *given* perturbation; second, to find a *self consistent* solution for the perturbation acting on all the electrons. Some general results concerning these two points are recalled in this section.

2.1. *Given Perturbation Acting on an Electron*

Let $V_0(\mathbf{r})$ be the periodic potential of an electron in the pure metal, $V(\mathbf{r})$ the potential of the perturbed lattice. The *perturbing potential* $V_P = V - V_0$ is here assumed to be given and to vary only with the position \mathbf{r} of the particle.

Some general properties may be stated about the number of states in a band (§ 2.1.1) and the influence of boundary conditions (§ 2.1.2). But the problem is usually so complicated that some approximations are necessary to compute the quantized states (§ 2.1.3).

2.1.1. *Energy Bands. Extended and Bound States*

When a perturbation is introduced into a lattice, well-known results of group and perturbation theories may be applied to study the grouping of the energies of the quantized electronic states into energy bands. These results are recalled here. The conclusions are summarized at the end of the section and illustrated by an example in one dimension.

(a) Keeping the boundary conditions constant and letting the perturbation V_P increase continuously from zero to its actual value, one displaces the energies of the quantized states *continuously, without altering their number* if degeneracy is taken into account (van der Waerden 1932): the quantized energy levels are continuous 'functionals' of the perturbing

potential (cf. Volterra 1930). If the wave function ψ of a given state corresponds to a perturbation V_P , an *infinitesimal* change δV_P of the perturbation alters its energy by †

$$\delta E = \int_V \delta V_P \psi^* \psi d\tau / \int_V \psi^* \psi d\tau, \quad (1)$$

which is thus proportional to the density $\psi^* \psi$ and to δV_P at each point.

(b) When the perturbed lattice has *no symmetry*, the degeneracies due to the symmetry of the initial lattice are removed by the perturbation: momenta and Brillouin zones lose their meaning; 'overlapping bands' (i.e. Brillouin zones with overlapping energy limits) lose their identity. Each state has an energy different from that of any other state, whatever the perturbation: the states do not 'cross' each other.‡

If V_P is *small*, the wave functions are little perturbed, and so extend through the lattice like the unperturbed ones. Equation (1) and the fact that they cannot cross shows that their energy varies quasicontinuously in each non-overlapping band or set of overlapping bands, which have nearly the same energy limits as for $V_P=0$.

With *stronger* but *localized* perturbations V_P , a few states may become tightly localized round the perturbation. According to (1), their energy varies much more rapidly with the perturbation than those of the extended states which build up the band structure. Not being able to cross the extended states, the *bound* states must have energies falling within one of the gaps of forbidden energies of the band structure.§

When the perturbation increases from zero, considerations of continuity show that any bound state comes from an extended state at a limit of the band structure, from which it is thus *subtracted*. The total number of states in a band or set of overlapping bands of the perturbed lattice is therefore increased or decreased each time a bound state is added or subtracted respectively by the perturbation.

Finally if the lattice extends to infinity and contains only a finite number of localized impurities, (1) shows that the band structure of extended states has exactly the same limits of energy as in the unperturbed lattice.

(c) There is no important change in these conclusions if the perturbed lattice retains *some symmetry*. The quantized states are divided into various sets having different symmetry properties and called 'irreducible representations of the symmetry group' of the perturbed lattice. The example below makes clear what these sets are. The states belonging to a

† Atomic units $e=m=\hbar=1$ are used throughout; V is the volume of the solid.

‡ Except for very special forms of V_P ('accidental' crossings).

§ Any localized increase of charge within the limits of the band structure must be a continuous function of the energy and extend over a finite range of energy. If this range is small, one has a so-called 'imaginary' or 'quasi' bound state well-known in the scattering of free electrons by localized perturbations (cf. Mott and Massey 1949).

representation are not degenerate and do not cross each other; but states belonging to different representations may cross each other.

Each degenerate state of the unperturbed lattice gives rise by linear combination of Bloch functions to states belonging usually to the various representations of the group of the perturbed lattice. Each band or set of overlapping bands thus splits into continuous subbands belonging to the various representations and having all nearly the same limits of energy if V_P is small.

When the perturbed lattice is still *periodic* (as for a superlattice), the degeneracy of momenta which is preserved splits each band into Brillouin zones. According to (1), the limits of these zones occur by resonance when the density has a common period with V_P .

(d) In the *conduction band* of a *metal*, the density $|\psi|^2$ of a Bloch function ψ is often nearly constant (Mott and Jones 1936). Then, from (1), and neglecting the small splitting of each degenerate state connected with cross terms

$$\int_V \psi_j^* V_P \psi_k d\tau,$$

the change of energy when V_P is introduced is

$$\Delta E \simeq V^{-1} \int_V V_P d\tau + O_2(V_P). \quad . \quad . \quad . \quad . \quad (2)$$

This does not depend on the momentum or the energy of the state: degeneracies connected with momenta, for instance the individuality of overlapping bands, are preserved; and this is a good approximation for states which are not bound to the perturbing field and thus not too near the limits of the band structure. Let n_0 and n be the densities of states per unit volume and unit energy in the pure and perturbed lattice; one has

$$n(E) \simeq n_0(E - \Delta E) + O_2(V_P). \quad . \quad . \quad . \quad . \quad (3)$$

Neglecting second order terms, the conduction band is only shifted by the average value of V_P , *without alteration of shape*.

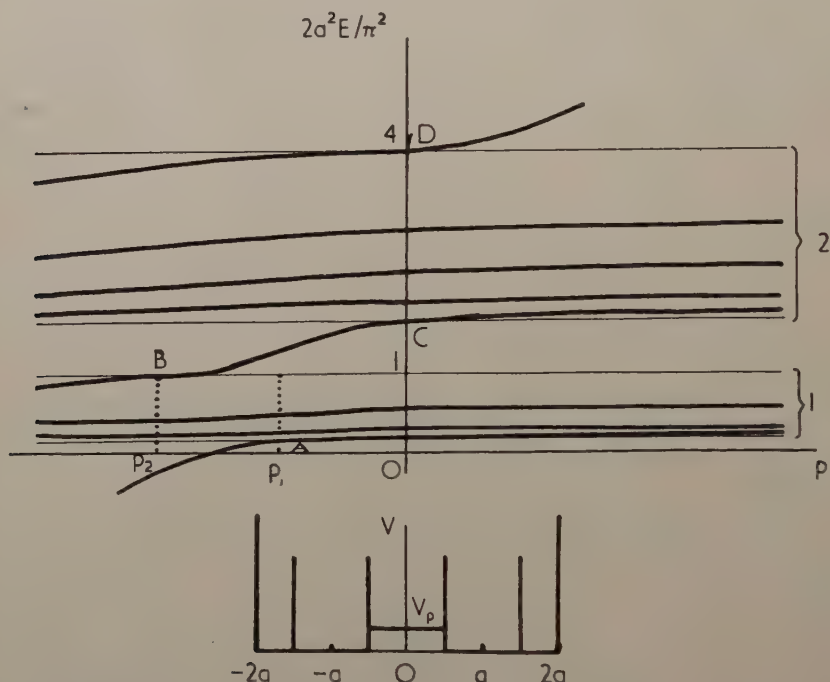
This approximation of 'rigid band structure' has been often used in the study of alloys since Jones' interpretation of Hume-Rothery's rules (1934).† The approximation is *not* valid for very narrow bands, near the limits of the band structure nor for large perturbations. Second order terms in (2) should be taken into account for larger V_P (cf. Shinohara 1952, 1954). General results are more readily obtained through another approximation (§ 4).

In conclusion, the band structure is deformed continuously with the perturbation and alterations are small for a small or localized perturbation. Neglecting second order terms, the conduction band of a metal is shifted

† The approximation of 'almost free electrons' sometimes used in pure metals (Mott and Jones 1936) is justified in a similar way; but V_P is then the whole potential acting on the conduction electrons, instead of the much smaller change of potential when an atom is substituted for another.

One verifies easily that there is one less state in the lowest band for $p_2 < p < p_1$ than for $p > p_1$. Figure 2 shows how states coming out of a band are subtracted from it. The states do not cross, the state with lowest energy in the band giving rise to the bound state for a sufficiently attractive perturbing field. The limits of the bands are not as precise in fig. 2 as in fig. 1, although states come out of the bands at exactly the same points A, B, C, D . . . in both cases. Finally, except for the states near to the limits of the bands, the slope of the curves for small V_P is nearly the same for all states, in agreement with (2).

Fig. 2



Perturbed and bounded Kronig and Penney lattice. Antisymmetrical states.

2.1.2. Boundary Conditions

The study of the individual perturbed states is difficult, and use will be made of a general result of wave mechanics, concerning the *local density*

$$\rho(E, \mathbf{r}) = \int^E \psi^* \psi n(E) dE$$

of the states with energy less than E quantized in a volume of *constant* potential. Laue (1914) showed that ρ is a constant $N_0(E)$ *independent of the boundary conditions* throughout the volume, except within distances of the boundaries smaller than the wave-length of the states with energy E .

$N_0(E)$ is of course the density per unit volume of *states* with energy less than E in a constant potential extending to infinity:

$$N_0(E) = \int^E n_0(E) dE. \quad (4)$$

This was proved † for arbitrary boundary conditions by taking ρ as the density of wave packets and may be directly extended to any *periodic* potential by using Bloch functions instead of plane waves. $\rho(E, \mathbf{r})$ is then a periodic function of \mathbf{r} with an average value equal to $N_0(E)$.

When a *localized* perturbation V_P is introduced into a metal, this result shows that the perturbed states rearrange themselves in such a way that the electronic density $\rho(E, \mathbf{r})$ is unaltered in the metal at large distances from the perturbation, a result often intuitively used. Use will be made of it when studying the screening provided by a metal and the corresponding displacement of the Fermi level (cf. § 2.2.2).

Laue's result justifies the Thomas-Fermi approximation (cf. Gombàs 1949). Its extension to periodic lattices is the basis of a generalization of this approximation used in § 2.1.3.

2.1.3. Approximations Used

The standard perturbation method has been used in some simple cases, but the degeneracy of the initial states make computations difficult, and more physical insight is often obtained by simpler methods, which are reviewed in this section.

2.1.3.1. *Perturbation Method.*—To solve the equation for an electron in the perturbed lattice

$$\Delta\psi_1 + 2(E - V_0 - V_P)\psi_1 = 0, \quad (5)$$

ψ_1 may be developed in terms of the Bloch functions $\psi_{n, \mathbf{k}}$ of all Brillouin zones n and momenta \mathbf{k} of the unperturbed lattice, which form a complete set:

$$\psi_1 = \sum_{n, \mathbf{k}} C_n(\mathbf{k}) \psi_{n, \mathbf{k}}. \quad (6)$$

The coefficients $C_n(\mathbf{k})$ are then given by

$$\Delta_{n, \mathbf{k}} C_n(\mathbf{k}) = 0, \quad (7)$$

$$\text{with } \Delta_{n, \mathbf{k}} = \sum_{n', \mathbf{k}'} \left\{ [E - E_{n', \mathbf{k}'}] \delta_{n'n} \delta(\mathbf{k}' - \mathbf{k}) \int_V \psi_{n', \mathbf{k}'}^* \psi_{n, \mathbf{k}} d\tau - \int_V \psi_{n', \mathbf{k}'}^* V_P \psi_{n, \mathbf{k}} d\tau \right\},$$

and the quantized levels E defined by $|\Delta_{n, \mathbf{k}}| = 0$. $E_{n, \mathbf{k}}$ is the energy corresponding to $\psi_{n, \mathbf{k}}$.

† Laue's result is more complete than the usual statement that the density $N(E)$ of *states* with energy less than E , quantized in a volume of constant potential, tends towards a value $N_0(E)$ independent of the boundary conditions when the volume or the energy E become infinite (cf. Weyl 1912, for reflecting boundaries of any form).

When V_P is nearly a constant, the integrals in V_P with $n' \neq n$ or $\mathbf{k}' \neq \mathbf{k}$ are small and may be treated as perturbations. The first order approximation is the eqn. (1) above. The second order approximation has been used to study the action of a constant electric field (Bloch 1929, Peierls 1933, Jones and Zener 1934) and the scattering of free electrons by a screened coulomb field $V_P = r^{-1} \exp(-qr)$ (Shinohara 1952, 1954). Slater and Koster studied recently (1954) the case where only one zone need be considered and

$$\int_V \psi^*_{\mathbf{k}'} V_P \psi_{\mathbf{k}} d\tau = \text{const.}$$

For states near to the limit of a zone or for rapidly varying perturbations, Bloch functions of more than one zone should however be used (cf. Adams 1952, 1953).

The calculations are usually complicated, owing to the number of wave functions involved in (6),† and simpler methods may be used for the conduction bands of insulators and of metals. These are reviewed later.

2.1.3.2. *Insulators* (Tibbs 1939).—Let w be the wave function of a free electron of energy $E - E_0$ scattered by V_P :

$$\Delta w + 2(E - E_0 - V_P)w = 0. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Then, if $\psi_0(E_0)$ is a Bloch function with energy E_0 ,

$$\psi_1 \simeq \psi_0(E_0)w$$

is an approximate solution of eqn. (5), which neglects a corrective potential $\delta V_P = -\nabla w \cdot \nabla \psi_0 / w \psi_0$. This is especially small if E_0 is the centre of an s zone with an effective mass near to unity: $\nabla \psi_0$ is then very small in nearly all the volume of the solid (cf. Mott and Jones 1937); $\nabla w / w$ is small, according to (8), if V_P varies slowly and $E - V_P$ is near to E_0 .

This justifies the treatment of conduction electrons in the alkali halides as free, and scattered by a potential V_P (Tibbs 1939, Mott and Gurney 1949) and, to a lesser degree, in mono- and polyvalent metals (Mott and Jones 1936), for there the Fermi level is rather far from the bottom of the band.

From the classical relation (Mott and Jones 1936)

$$\int_V \psi_0^* \nabla \psi_0 d\tau \bigg/ \int_V \psi_0^* \psi_0 d\tau = i \nabla_{\mathbf{k}} E_0. \quad . \quad . \quad . \quad . \quad (9)$$

where $\nabla_{\mathbf{k}}$ denotes the gradient in momentum space, it is seen that in general the best choice for E_0 is the stationary value in momentum space ($\nabla_{\mathbf{k}} E_0 = 0$) nearest to the average value of $E - V_P$. The approximation is of course not so good for bands with symmetry other than s (germanium,

† Using a Fourier transform, eqn. (7) may be translated into the so-called 'Wannier functions' (Wannier 1937, Slater 1949, 1953, Adams 1952), but without much simplification of the actual computations except for narrow bands, where however a direct tight binding method seems preferable.

silicon . . .) or effective mass μ different from unity. In this last case, the approximation is *not* improved by introducing μ in eqn. (8), as was suggested by Peckar (1946, cf. Friedel 1954 b, d). The approximation is especially good for states bound to the perturbation, for which $E - V_P - E_0$ is zero in a region where their density is very large.

2.1.3.3. *Metals*.—If V_P is a constant, the densities $\rho_0(E, \mathbf{r})$, $\rho(E, \mathbf{r})$ of electrons with energies less than E in the pure and perturbed solids are related by

$$\rho(E, \mathbf{r}) = \rho_0(E - V_P, \mathbf{r}). \quad (10)$$

When V_P varies with \mathbf{r} , this relation is still approximately valid, according to § 2.1.2, in the regions where V_P varies little within the wave length of the electrons with energy $E - V_P$. This is analogous to the Thomas–Fermi approximation for free electrons. It is a good approximation only when V_P varies slowly in space and when the energy $E - V_P$ is not too near to the limit E_0 of a band; it is thus better for the conduction electrons of a metal than for those of a semi-conductor, and very bad for bound states. Writing that V_P varies by less than the distance of $E - V_P$ to the nearest band limit E_0 over the wave length of the electrons with energy $E - V_P$, the following condition is obtained:

$$|\nabla V_P| < (2\mu)^{1/2} |E - E_0 - V_P|^{3/2}, \quad (10^{\text{bis}})$$

where μ is the ‘effective’ mass in the band. This condition is satisfied almost everywhere for conduction electrons and the perturbation $V_P = -Zr^{-1} \exp(-qr)$ studied in this paper; for (10^{bis}) is satisfied at distances r larger than the small value $(2\mu Z)^{-1}$.

Finally, for large perturbations, it is sometimes useful to take some average value of the local changes in potential and kinetic energies. This method, due to Mott (1936) will be described when studying alloys belonging to different lines of the periodic table (§ 2.2.3).

In conclusion, the Thomas–Fermi approximation will be used through most of this paper, although Tibbs’ method will be of use for studying bound states or when data on wave functions are required in the conduction band of mono- and polyvalent metals. In both cases, *corrections* should be made when V_P varies rapidly in space, as is usual in actual cases.

2.2. Self Consistent Solution in an Alloy

In metallic substances, all the conduction electrons of the solid must be studied together in a self consistent way: the perturbing potential V_P acting on one electron is not known *a priori*, but is partly due to the perturbation of the other conduction electrons. This difficulty has been only partly solved so far. We describe two simple approximations related to the methods of ‘molecular’ and ‘atomic’ orbitals of chemistry, then stress a necessary condition for the screening of the potential acting on the electrons at the Fermi level. Substitutional alloys of elements belonging to different rows of the periodic table are considered.

2.2.1. *Molecular and Atomic Orbitals*

It is usually assumed that the valency electrons of all the elements in the alloy move in the *same* potential.

In the usual Hartree approximation, V_P is due to the change of ion core potential and to the total change of electronic density of the conduction electrons when the impurity is introduced. This is similar to the method of *molecular orbitals* (Hund-Mulliken approximation), and has the advantage that all the electrons are described by orthogonal wave functions. When computing the total energy, provision must be made for the fact that the sum of the quantized energies of the individual electrons includes *twice* the self interaction of the change of density in the conduction band. This correction is large when the charge displaced by V_P is large and concentrated.

When V_P is attractive enough to accept bound states below the bottom of the conduction band, the corresponding electrons are treated as moving in the field of their own charge, obviously a rather bad approximation. This point emphasizes the fact that, with large displacements of charge in the conduction band, the change of *correlation* is important, especially for slow electrons. Correlation is difficult to take into account by this method, and the total energy of the alloy is not reliably computed in this way. The method is however good for *fast* electrons, for which correlation effects are small (cf. § 3).

To compute the *energy* of the system, a more direct method is to assume that the impurity dissolves as a neutral atom if in an interstitial position (H in copper) or as an ion with the same valency as the matrix if in a substitutional position (Zn^+ , Ga^+ , Ge^+ . . . for Cu⁺). The valency electrons assumed in *atomic orbitals* bound to the impurity are treated in the potential of the impurity alone (the fields of their own charge and of the conduction electrons excluded) and the density and energy of the conduction electrons are assumed little perturbed by the introduction of the impurity. This approximation perhaps takes a better account of the correlation terms for large displaced charges, and has been used to compute the energy of formation of alloys (§ 4). For substitutional alloys, the method is only applicable to impurities with valencies larger than that of the matrix. In this approximation, electrons in atomic orbitals and in the conduction band move in *different* potentials and therefore are described by non-orthogonal wave functions; also there should be strong correlation between the positions of these electrons. Both considerations cast some doubt upon the validity of the approximation.

2.2.2. *Screening. Displacement of the Fermi Level*

When an additional nuclear charge Z is introduced into a *pure* metal, its coulombian potential $-Zr^{-1}$ must be screened at small distances by a local heaping up of charge from the conduction band: this is a well-known consequence of the high conductivity of the metal. When Z electrons are also introduced, so as to preserve the electrical neutrality of the metal, the

perturbation V_P is thus localized around the point charge Z . The major part of the matrix is unperturbed; it must thus have *exactly* the same Fermi level as the pure metal, for it has the same electronic density (cf. § 2.1.2); this remains true as long as the impurities do not interact, so that they all preserve the same potential V_P : a change of Fermi level would correspond to a change of electronic density in the matrix, and thus to a supplementary potential.

More quantitatively, the approximation (10) is valid at large distances \mathbf{r} from the impurity, for the electrons at the Fermi level. In either approximation of the previous paragraph, the total charge locally displaced in a sphere of radius R of metal is thus

$$Z_0 = 4\pi \int_0^R [\rho(E_M + \Delta E_M, \mathbf{r}) - \rho_0(E_M, \mathbf{r})] r^2 dr \propto \text{const} + \int_0^R (\Delta E_M - V_P) r^2 dr,$$

where ΔE_M is the change of Fermi level, and the finite constant comes from the fact that the approximation (10) is not exact at short distances.

The charge displaced in a metal extending to infinity thus remains finite only if $\Delta E_M = 0$ and if

$$\int_0^\infty V_P r^2 dr$$

is finite: the coulombian potential $-Zr^{-1}$ must be totally screened, so that V_P decreases more rapidly than r^{-2} .

For finite concentrations c , thus one solute atom in each sphere of metal of finite radius $R \simeq r_s c^{-1/3}$, a finite ΔE_M would correspond to a finite change of density $\delta\rho \propto \Delta E_M$ leading to a supplementary potential $V_P \propto \Delta E_M (R^2 - r^2/3)$. This in its turn would displace a charge $\delta Z_0 \propto \Delta E_M R^5 + \text{const}$ which could go to zero for R infinite only if $\Delta E_M R^5$ remains finite. The Fermi level thus changes by an amount at most proportional to the power $\frac{5}{3}$ of the concentration c of impurities.

Screening and Fermi level will be studied more exactly in § 3.3.

2.2.3. Large Supplementary Charges

When the constituents of a substitutional alloy belong to different rows of the periodic table, the perturbation V_P is too large to be treated by one of the methods of § 2.1.3. One usually represents the impurity in this case as an extra charge of amount equal to the difference between its *valency* and that of the matrix. This assumes that the dissolution into each other of two elements with the same valency does not perturb the conduction band very much, except for a change in the number of nodes of the wave functions. It is probably a good approximation for heavy elements (Mott 1936).

When for instance a gold atom is substituted for a silver one, the wave function at the bottom of the conduction band is almost the same as in pure gold in the atomic polyhedron of the gold atom: it moves in the same field of potential if the $5s^2$, $5p^6$, $5d^{10}$ electrons of Au are treated in 'atomic' orbitals and if the polarization of the conduction band is neglected;

it has almost the same boundary conditions and the same energy: the change in kinetic energy (one more node than around Ag atoms) compensates for the large increase in potential energy. In the Wigner-Seitz approximation, the wave functions of the conduction electrons in the alloy are thus practically the same as in pure silver, but for the introduction of one more node around each gold atom. Except for this node, Hg, Tl, Pb . . . behave in the same way as Cd, In, Sn . . . when dissolved in silver. A similar case is pictured in figs. 1, 2: for $-p$ somewhat larger than $-p_2$, the first band has the same energy distribution as for $-p$ small; the wave functions have one more node near the impurity, due to the bound state below.*

In this approximation, the energy of solution of gold in silver is zero. The conduction electrons of the alloy are actually slightly scattered, due to the difference of the energy E_0 of the bottom of the conduction band in pure solute and solvent (Mott 1936); they tend to concentrate on the element with the lower energy E_0 (Huang 1948), at the expense only of the neighbouring atoms, for there must be no net displacement of charge at large distances (cf § 2.2.2); this *polarization* of the conduction band makes the alloy more stable, thus giving rise to a small negative energy of solution (-0.15 eV per atom for **Ag Au**†).

A *vacancy* can then be treated as an impurity with *zero valency* (cf. Dexter 1952). This is probably better than to treat the potential V_p as a small perturbation, as was done by Huntington (1942). A large correction is however to be expected, because of the large number of nodes suppressed from the wave functions around the impurity.

§ 3. MOLECULAR ORBITALS. FIRST ORDER APPROXIMATION

The purpose of this and the next sections is to compute the self-consistent potential around a point charge Z introduced into a metal. Z is the nuclear charge of an interstitial impurity (1 for **Cu H**) or the difference of valency of a substitutional impurity with the matrix (1 for **Cu Zn**, **Cu Cd**). All the conduction electrons are treated as in 'molecular' orbitals moving in the same field of potential. The distortion of the lattice due to a difference in size of the various atoms is neglected.

Mott (1936) studied this problem for a gas of free electrons using a *first order* approximation. This method is extended to more complicated band structures and to finite concentrations. Its relations with Born's classical approximation and with Jones' model of rigid bands (§ 2.1.1) are stressed. A correction for exchange is introduced. These points are illustrated by studying some properties of alloys. Better approximations will be developed in § 4.

The basic assumptions of the method will next be analysed.

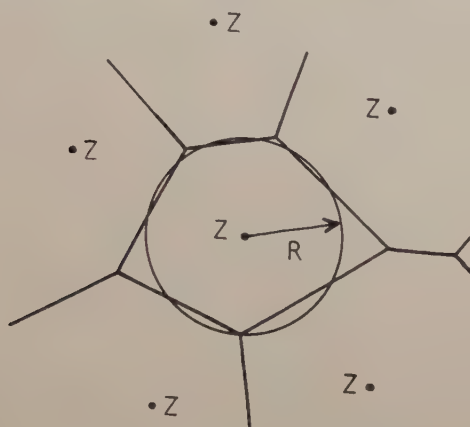
* For similar reasons, the Ramsauer-Townsend effect of *free* electrons varies periodically with the atomic number of the scattering atoms (Mott and Massey 1949).

† **AB** means B dissolved into A.

3.1. Assumptions of the Method

The metal is divided into polyhedra, each containing an impurity atom at its centre (fig. 3). The following approximations are made :

Fig. 3



Finite concentration of impurities.

1. The polyhedra are replaced by spheres of the same volume. All the spheres are assumed to have the same radius R (well dispersed impurities).

2. Hartree averages are made, correlation terms being thus neglected. Poisson's equation then gives, with the notation of § 2.2.2,

$$\Delta V_P = -4\pi[\rho(E_M + \Delta E_M, \mathbf{r}) - \rho_0(E_M, \mathbf{r})], \quad . \quad . \quad . \quad (11)$$

with the following boundary conditions for V_P :

$$\begin{aligned} V_P &\rightarrow -Zr^{-1} && \text{when the distance } r \text{ to the charge } Z \rightarrow 0, \\ V_P &= dV_P/dr = 0 && \text{for } r=R. \end{aligned} \quad . \quad . \quad . \quad . \quad (12)$$

The last condition is by reason of symmetry at the boundary of two polyhedra; the preceding one ($V_P(R)=0$) comes from the neutrality of the sphere if Z electrons are introduced into the metal together with each charge Z , so as to preserve the neutrality of the metal.*

3. The generalized Thomas-Fermi approximation (10) is used. Thus

$$\Delta V_P \simeq -4\pi[\rho_0(E_M + \Delta E_M - V_P, \mathbf{r}) - \rho_0(E_M, \mathbf{r})]. \quad . \quad . \quad . \quad (13)$$

This equation, together with conditions (12), allows in principle $V_P(\mathbf{r})$ and ΔE_M to be computed when the electronic density $\rho_0(E, \mathbf{r})$ in the pure metal is known.

4. A first order approximation in $\Delta E_M - V_P$, assumed to be small, gives

$$\Delta V_P \simeq 4\pi(V_P - \Delta E_M)\partial\rho_0(E_M, \mathbf{r})/\partial E_M. \quad . \quad . \quad . \quad . \quad (14)$$

* The absolute zero of energy used throughout is that of an electron at rest and at infinity outside the solid.

5. A constant density $|\psi|^2$ in space is assumed for electrons in states at the Fermi level in the pure metal. This is certainly a good approximation for the mono- and polyvalent metals with a conduction band of effective mass near to unity (cf. Mott and Jones 1936). It will be applied even to transitional metals like nickel with a relatively narrow d band: d electrons should be only a little more concentrated near the nuclei, for the width of a band is very sensitive to this concentration.†

$\partial\rho_0/\partial E_M$ may then be replaced by the density of states $n_0(E_M)$ of the band structure

$$\Delta V_P \simeq 4\pi n_0(E_M)(V_P - \Delta E_M). \quad (15)$$

Conditions 4 and 5 show that the model of a rigid band structure is applicable.

It is now easy to compute the self consistent solution for V_P .

3.2. Self Consistent Perturbation

For one impurity dissolved in a metal extending to infinity (R_∞), (12) and (15) give

$$V_P = -Zr^{-1} \exp(-qr), \quad (16)$$

with

$$q^2 = 4\pi n_0(E_M) \quad \text{and} \quad \Delta E_M = 0. \quad (17)$$

The Fermi level is unchanged because the coulombian field of the impurity is screened (cf. §2.2.2). The radius of screening, a small multiple of q^{-1} , is a function only of the density of states $n_0(E_M)$ of the pure metal, a quantity proportional to the specific heat at low temperatures (cf. Mott and Jones 1936). The radii q^{-1} deduced in this way ‡ for usual metals are near one ångström: the screening is concentrated round the impurity atoms and does not much overlap the atoms of the matrix.

With a parabolic conduction band, effective mass μ and maximum occupied momentum k_M , $n_0 = \mu k_M / \pi^2$ and

$$q^2 = 4\mu k_M / \pi. \quad (18)$$

In the usual metals treated, μ and k_M and thus q^{-1} are of the order of the atomic unit: for copper, $k_M = 0.725$, $\mu \simeq 1.4$ (Seitz 1940), thus $q = 1.1_5$ atomic units.

For finite concentrations of impurities (R finite), the solution is somewhat more complicated (cf. Friedel 1953 c):

$$V_P = \Delta E_M - \frac{Z}{r} \frac{qR \cosh\{q(R-r)\} - \sinh\{q(R-r)\}}{qR \cosh qR - \sinh qR} \quad (19)$$

† In the tight binding approximation, the width of the band is proportional to an overlap integral $\int V\psi^*\psi d\tau$, where both the potential V and the volume of integration decrease with the electronic density $\psi^*\psi$ at the mid point between two atoms (Seitz 1940).

‡ The usual formula of the band approximation neglects the correlation terms. This introduces an error probably smaller than 10% (cf. Bohm and Pines 1953).

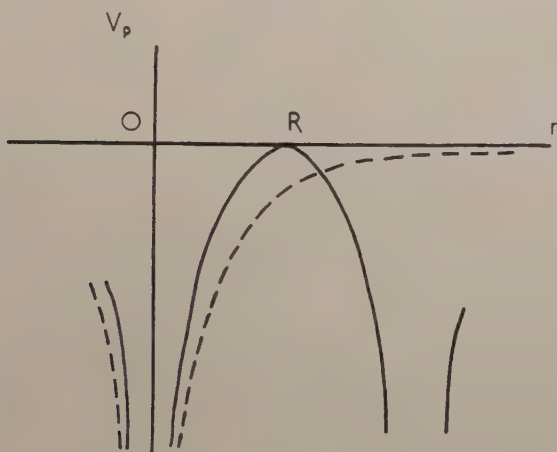
with

$$\Delta E_M = Zq/(qR \cosh qR - \sinh qR).$$

The displacement of the Fermi level may be interpreted as follows: V_P vanishes at a distance R instead of at infinity and is thus weaker (fig. 4). The charge displaced below E_M is therefore smaller than Z , and the difference z must be made up by the displacement ΔE_M of the Fermi level. The charge displaced by V_P below E_M in a sphere of radius r is, in the approximations of § 3.1,

$$Z_0(r) = \int_0^r [\rho(E_M, \mathbf{r}) - \rho_0(E_M, \mathbf{r})] 4\pi r^2 dr = -4\pi n_0(E_M) \int_0^r V_P r^2 dr. \quad (20)$$

Fig. 4



Perturbation V_P at finite concentration (for $Z > 0$). Punctuated line: for infinite dilution.

With (17), (19), one finds

$$z = Z - Z_0(R) = \frac{1}{3} q^2 R^3 \Delta E_M. \quad (21)$$

This is indeed the charge necessary to raise the Fermi level by ΔE_M .

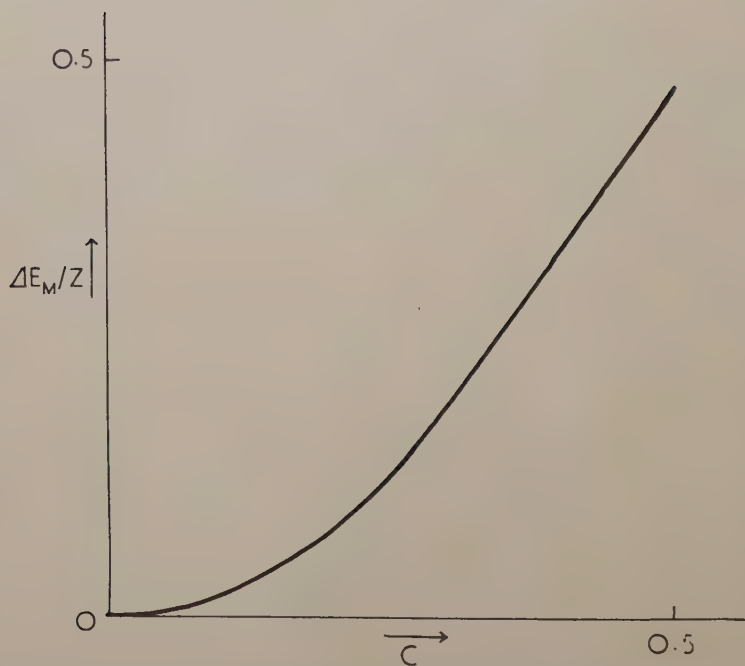
Figure 5 gives $\Delta E_M Z$ for varying atomic concentrations c for copper. Figure 6 gives $z Z$ as a function of $(qR)^{-3} = (qr_s)^{-3} c$ (r_s radius of the atomic sphere). For the usual metals $(qr_s)^{-3} \simeq 0.01$ to 0.05 .

Some simple consequences of the equations obtained are stressed in the following paragraphs.

3.3. Range of Interaction for Impurities

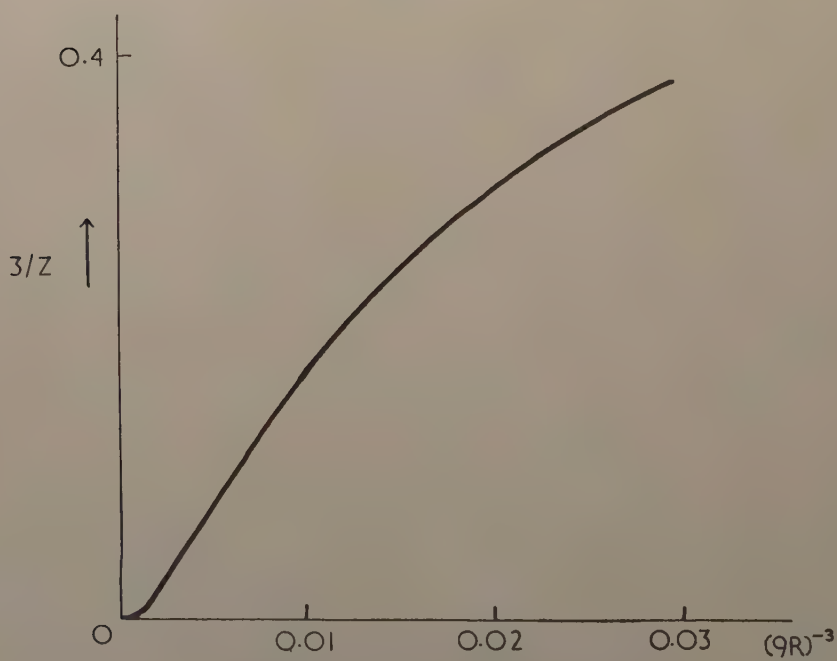
The curves fig. 5 and 6 have *zero slope* at the origin: the screening is localized and the Fermi level is constant for small concentrations where impurities do not interact but are separated by a fair amount of unperturbed solvent. This was predicted in § 2.2.2.

Fig. 5



Displacement ΔE_M of the Fermi level with concentration c for copper (in ev).

Fig. 6



Variation of the delocalized screening z .

The figures show that the impurities *interact* appreciably for $qR < 10$, thus at a concentration

$$c_0 > (qr_s/10)^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The maximum distance of interaction between impurity atoms $2R_0 \simeq 20q^{-1}$ corresponds to a radius R_0 of almost total screening at infinite dilution. For (16), (17) and (20), give for the screening charge $Z_0(R_0)$ within a radius R_0

$$\epsilon = 1 - Z_0(R_0)/Z = (1 + qR_0) \exp(-qR_0).$$

This is negligible for $R_0 > 10q^{-1}$: $\epsilon = 10^{-3}$ for $R_0 = 9q^{-1}$; $\epsilon = 5 \times 10^{-5}$ for $R_0 = 10q^{-1}$.

Typical values of R_0 and c_0 are given in the following table:

| | Cu | Al | Tl | Fe | Ni |
|-----------|------|-----|-----|-----|------|
| q | 1.13 | 1.4 | 1.0 | 3.2 | 4.75 |
| R_0/r_s | 3.3 | 2.4 | 2.8 | 1.2 | 0.8 |
| c_0 % | 3 | 7.5 | 4.5 | 60 | >100 |

The values of q were computed by (17) from experimental values of the densities $n_0(E_M)$ (Mott 1952).

For such metals as Cu Al, etc., c_0 is a few per cent and R_0 of the order of *several* interatomic distances. R_0 is reduced somewhat when a correction for exchange is introduced (cf. § 3.7.3), and the better approximations of § 4 would give a value of R_0 smaller for positive than for negative Z . It seems nevertheless a rather rough approximation to consider interaction only between nearest neighbours in alloys like **Cu Zn**. This approximation is better for alloys with metals of higher valencies (large k_M , eqn. (17)).

The concentration c_0 found for Tl agrees with Bloembergen and Rowland's measurement of the nuclear 'Knight shift' of Tl atoms in **Tl Sn** alloys (1953). This shift is proportional to the s part of the density $\partial\rho(E_M + \Delta E_M, \mathbf{r})/\partial E_M$ at the Tl nuclei; up to 3% of Sn atoms it remains practically unaltered, so that ΔE_M must vanish and there must remain a fair proportion of unperturbed Tl atoms.

In transitional metals like Fe, Ni (large μ), the radius of screening is of the order of the interatomic distance: the solute elements interact only when c is quite large and very weakly (almost random solution). In alloys of two transitional metals with the same crystal structure,* the solute and solvent atoms are therefore almost in the same state as in the pure component: *the energy ϵ of formation of the alloy is very small*. When a solution is random and with $\epsilon=0$, it is said to be 'ideal'. This is

* And with the approximation (19) valid up to $c=1$.

practically the case for alloys of iron with transitional metals (Barrett 1953); the case of Ni in γ iron has been studied recently (Oriani 1953).

3.4. Delocalization of the Screening

The charge $Z-z$ displaced below E_M is strongly *localized* around the impurity. For the density of charge producing it, namely

$$\frac{1}{4\pi r^2} \frac{dZ_0}{dr} = -\frac{1}{4\pi} n_0(E_M) V_P(r),$$

vanishes, together with its derivative at the limit $r=R$ of the polyhedra (cf. (12)).

The complementary screening z has on the contrary a *uniform* density. Figure 6 shows that even at large concentrations z/Z remains much *smaller than unity*; thus the conduction electrons have a density far from uniform.

This agrees with the small stability of superlattices in alloys like β brass: if the conduction electrons had a uniform density ($z=Z$), the difference of charge of the inner Cu^+ and Zn^{++} ions would lead in the ordered state to a stable ionic compound with a large Madelung energy. From the small observed energy of the order-disorder transformation, Mott (1937) deduced on the contrary that $z \sim 0.15$. Equation (21) gives in this case $z=0.25$, the right order of magnitude. The correction for exchange of § 3.7.3 gives an even smaller value: $z=0.10$ for $\mu=1$.

3.5. Density of States. Rigid Band Structure

The density of states with energy less than E in the alloy is using the approximation of § 3.1,

$$\begin{aligned} N(E) &= V^{-1} \int_V \rho(E, \mathbf{r}) d\tau = V^{-1} \int_V \rho_0(E - V_P, \mathbf{r}) d\tau \\ &= N_0(E) - n_0(E) \cdot V^{-1} \int_V V_P d\tau = N_0 \left(E - V^{-1} \int_V V_P d\tau \right). \quad (23) \end{aligned}$$

The band structure thus *preserves its form* and is shifted as a whole in the energy scale by the average perturbation

$$E_0 = V^{-1} \int_V V_P d\tau,$$

a general result for metals when second order terms in the perturbation are neglected (cf. § 2.1.1(d)). This is pictured in fig. 7. The approximation is *not* valid near to the bottom of the conduction band, where bound states subtracted from the band may appear (§ 2.1.1).

The model of rigid bands is useful when studying the density of states at the Fermi level or the displacement $\delta E = -E_0 + \Delta E_M$ of the Fermi level *relative* to the band structure.* This will appear in the following paragraphs.

* One must keep in mind that the displacement ΔE_M of the Fermi level in the absolute energy scale is smaller than δE , and vanishes at small concentrations.

The value of δE for a concentration c of impurities Z is given, from (23), by :

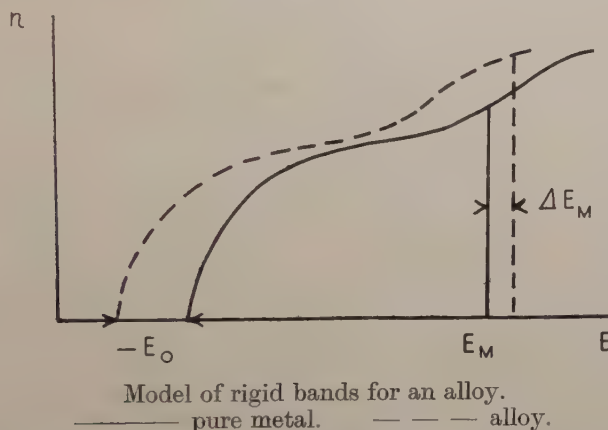
$$N_0(E_M + \delta E) - N_0(E_M) = cZ/v \simeq n_0(E_M) \delta E \quad (24)$$

(v is the atomic volume). The density of states at the Fermi level is altered through alloying by a factor

$$\frac{n_0(E_M + \delta E) - n_0(E_M)}{n_0(E_M)} = \frac{cZ}{v} \left(\frac{\partial n_0}{\partial E} \right)_{E_M} \quad (25)$$

For a parabolic conduction band with p electrons per atom, this is equal to $cZ/3p$. This equation could be checked by measuring low temperature specific heats of simple alloys. An improved formula is given in § 4.

Fig. 7



Jones' model of a rigid band structure and Mott's picture of localized screening are therefore *not* contradictory; they apply in energies and space respectively the same approximation of the first order in V_P . The case of overlapping bands will be treated in § 3.6 as an example of this point.

3.6. Overlapping Bands. Ferromagnetic Alloys

The model of rigid bands shows that the number of the Z extra electrons introduced with each impurity which go into the various bands which overlap at the Fermi level is *proportional to their respective densities of states* $n_0(E_M)$.

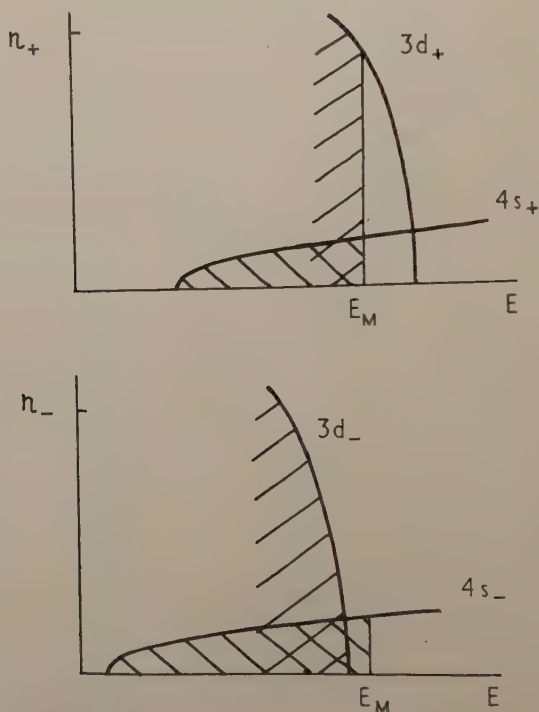
Mott (1935, 1953), Slater (1936) and others explained in this way the magnetic moments of *ferromagnetic alloys* by assuming that the ferromagnetic splitting of the band structure produces at the Fermi level very different densities of states n_+ , n_- for the two spin directions. Figures 8 and 9 recall the band structures proposed for nickel, cobalt and iron respectively. In both cases, one half only of the narrow 3d band has a large density of states at the Fermi level, the other being full in Ni, Co and presenting in Fe a minimum in the density at the Fermi level. Measurements of specific heats at low temperature (giving $n_+ + n_-$, cf. Seitz 1940) and optical absorption (giving $n_s \simeq 2n_+$, cf. Meier 1910) show that $n_+/n_- \sim 60$ for nickel and cobalt; a somewhat smaller value is probable in iron for n_-/n_+ .

The supplementary Z electrons per impurity atom would thus practically all go into the band structure with larger density, reducing by Z the excess of electrons of one spin in Ni, Co, and increasing it by Z in Fe. The *average* magnetic moment μ per atom of alloy therefore varies linearly with the concentration c of solute element

$$\mu = \mu_A + \alpha c Z \mu_0, \quad \dots \dots \dots (26)$$

with $\alpha = 1$ for Fe and $\alpha = -1$ for Co and Ni (μ_A is the magnetic moment of

Fig. 8



Assumed band structure for ferromagnetic nickel and cobalt.

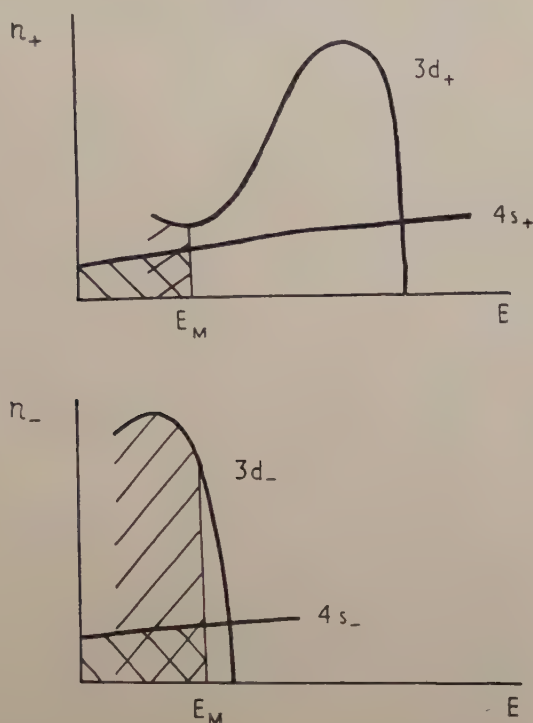
the matrix, μ_0 the Bohr magneton). These two straight lines are well known results of experiment, valid when Z and c are not too large (fig. 10).

Now it is equivalent to say that each overlapping band contributes to the screening of an impurity Z by an amount given by

$$Z_j = \int_0^R [\rho_j(E_M + \Delta E_M, \mathbf{r}) - \rho_{0j}(E_M, \mathbf{r})] 4\pi r^2 dr = n_{0j}(E_M) \int_0^R (\Delta E_M - V_P) \\ \times 4\pi r^2 dr = n_{0j}(E_M) Z / n_0(E_M),$$

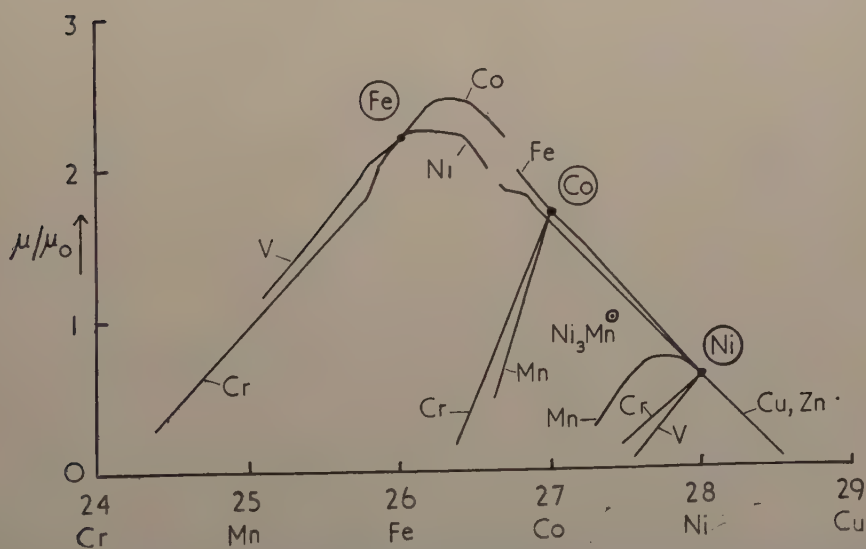
which is proportional to its density of states $n_{0j}(E_M)$. But from this point of view it is possible to go further and predict the respective magnetic moments μ_A , μ_B of the *solvent and solute atoms*. In alloys of transition metals even at high concentrations the screening is *localized* and concentrated on the solute atoms, because the density $n_0(E_M)$ is very large

Fig. 9



Assumed band structure for ferromagnetic iron.

Fig. 10



Atomic moments of the ferromagnetic elements and their alloys (after Slater, Pauling, Bozorth).

(cf. § 3.3). It is produced by that half of the band structure with much the higher density at the Fermi level,* and thus gives to the solute atoms a magnetic moment

$$\mu_B = \mu_A + \alpha Z \mu_0 \quad . \quad . \quad . \quad . \quad . \quad (27)$$

(α as in (26)), while leaving unchanged that of the matrix.

The magnetic moments μ_A, μ_B of some alloys as deduced from neutron diffraction (Shull 1953) are given in the following table, in Bohr magnetons† :

| A | B | | μ_A | μ_B | α_{exp} |
|-----------------|----|---------|---------|---------|-----------------------|
| Ni ₃ | Fe | disord. | 0.6 | 2.6 | -1.0 |
| | | ord. | 0.7 | 2.8 | -1.1 |
| Ni ₃ | Mn | ord. | 0.3 | 3.3 | -1.0 |
| Fe | Co | ord. | 1.7 | 2.8 | -1.1 |
| (Fe | Cr | disord. | 2.2 | 0.7 | +1.5) |
| (Co | Cr | disord. | 1.7 | 1.0 | +0.35) |

The accuracy claimed is 0.1 to 0.2 μ_0 . As μ_A is 0.6, 1.7 and 2.2 for pure Ni, Co, Fe respectively, a satisfactory agreement with (26) is obtained for Ni₃ Fe, Ni₃ Mn, Fe Co.‡ Ordering does not affect appreciably the results for Ni₃ Fe, as expected : the Fe atoms do not interact very much (cf. § 3.4).

The values given for **Fe** Cr and **Co** Cr are only one of two possible interpretations of the data. For **Fe** Cr, α has the sign predicted by (27) but is somewhat too large. For **Co** Cr, Z is probably too large for the approximations made here to be valid ; the case will be considered in § 4.

3.7. Energies of Solution. Interaction between Impurities

Energies of solution are not easily evaluated in this approximation, although the energy of formation of a vacancy has been computed in this way (cf. § 3.7.2). The change with concentration of the energy of dissolution is connected with the interaction between impurities ; its quantitative study needs some account to be taken of the correlation between electrons.

* In nickel or cobalt alloys, the 4s electrons may be said to be much less easily perturbed than the slower and heavier 3d 'positive holes' (cf. Goldman 1953, Friedel 1954 c). However, in a better approximation the s and d bands would lose their identity and only states with different spin directions can be treated independently (cf. § 2.1.1).

† Somewhat more accurate data have been obtained since (Shull 1954).

‡ The smaller magnetic moment of Ni in Ni₃ Mn is possibly related to a decrease in the number of 4s electrons : the lattice of Ni₃ Mn is expanded by 3% with respect to that of Ni (Kaya and Kussmann 1931), and this should displace the s band towards higher energies without affecting the d band very much. Krutter's computations on Cu illustrate this effect (cf. Seitz 1940). This expansion is related to the size effect, neglected in this section.

3.7.1. Energies of Solution

The energy of formation ϵ per atom of an alloy $A_c B_{1-c}$ is usually defined by the relation

$$cA_{\text{met}} + (1-c)B_{\text{met}} = A_c B_{1-c} + \epsilon. \quad (28)$$

The *energy of solution* ϵ_A per atom A dissolved will be defined here as the derivative of ϵ

$$\epsilon_A = d\epsilon/dc,$$

and thus by the following cycle, N being a large number:*

$$A_{cN-1}B_{(1-c)N} + A_{\text{met}} = A_{cN}B_{(1-c)N-1} + B_{\text{met}} + \epsilon_A. \quad (29)$$

For small concentrations c , solute atoms do not interact (§ 3.3); the energy ϵ_A needed to introduce a solute atom does not depend on c and ϵ is *proportional* to c . The approximations of this section are *not* very suitable to compute the initial slope of ϵ , especially for large Z : the interaction of V_P with the screening charge and the change in kinetic energy of the conduction electrons are both neglected as being of the second order in V_P (cf. eqn. (2)); changes in correlation terms are neglected (cf. § 2.2.2); finally the cycles used remove all its valency electrons from the solute element, thus giving the energy of solution as the difference of two large quantities. It is therefore not surprising that the energies of solution computed in this way for zinc in copper, cadmium in silver and mercury in gold are much too large, about +4 eV per atom, instead of a fraction of an electron volt as observed.

3.7.2. Vacancies

The energy of creation of a vacancy in a monovalent metal has been computed in the same way by Fumi (1954), assuming that it is equivalent to an impurity with $Z = -1$ (cf. § 2.2.3). He used the following cycle:

1. Remove a monovalent ion at the centre of a sphere of metal, and spread the corresponding unit charge uniformly in the sphere so as to compensate the field of the corresponding valence electron. The metal is still electrically neutral; the conduction electrons are perturbed by a localized potential V_P which repels locally a charge unity:

$$-n_0(E_M) \int_0^R 4\pi V_P r^2 dr = -1.$$

The total expenditure of energy is, from eqn. (2),

$$E_1 = N_0(E_M) \int_0^R 4\pi V_P r^2 dr = N_0(E_M)/n_0(E_M), \quad (30)$$

if $N_0(E_M)$ is the density of conduction electrons. For free electrons, $E_1 = \frac{2}{3}E_F$, if E_F is the width of the conduction band.

* Experimental data are more usually interpreted in terms of a quantity ϵ'_A such that $A_{cN-1}B_{(1-c)N} + A_{\text{met}} = A_{cN}B_{(1-c)N} + \epsilon'_A$. The Duhem-Margules relation (Kubaschewski and Evans 1951) gives

$$\epsilon_A = \epsilon'_A/(1-c) - \int_0^c \epsilon'_A d[c/(1-c)];$$

thus $\epsilon'_A \rightarrow \epsilon_A$ when $c \rightarrow 0$.

2. Expand the sphere of metal by an atomic volume and concentrate into the added spherical shell of metal the charge of the removed ion so as to compensate the local electronic density. The potential energy of the conduction electrons is thus kept constant, and their total kinetic energy, being proportional to $V^{-2/3}$, is reduced by

$$E_2 = -\frac{2}{3} \cdot \frac{3}{5} E_F = -\frac{2}{5} E_F.$$

The surface energy of the metal is not appreciably increased. The energy necessary to create a vacancy and put the atom back on the metal is therefore

$$E_V = E_1 + E_2 = \frac{4}{15} E_F.$$

This admittedly rough estimate seems in rather striking agreement with experiment, as the following table shows :

| Metal | Li | Na | K | Rb | Cs | Cu | Ag | Au |
|--------------|------------------|------------------|------------------|-----|-----|---------|------------------|-----|
| E_V comp. | 1.2 ₅ | 0.8 ₅ | 0.5 ₅ | 0.5 | 0.4 | 1.9 | 1.4 ₅ | 1.5 |
| E_V exper. | | 0.45(0.25 ?) | 0.25 | | | 1.2±0.1 | 1.3 | 1.3 |

The energies are expressed in ev. The experimental values for Cu, Ag, Au are deduced from various experiments (cf. Broom 1954, Koehler 1954). The more uncertain values for Na and K are deduced from the anomalies in resistivity and specific heat near the melting point (Carpenter 1953, Pochapsky 1953, McDonald 1953) and may possibly be due to other imperfections like interstitials or ‘crowdions’. The corresponding values for polyvalent metals are much too high, possibly owing to neglect of the correlation energy. Fumi estimated recently that the relaxation of the d shells reduces the computed energy by 0.4 ev in copper.

The computed energy does not depend on the actual form taken for V_P . It is unaffected by the exchange correction which will now be made before studying the energies of dissolution at larger concentrations.

3.7.3. *Exchange Correction*

The changes in exchange and coulomb correlation between electrons have been neglected so far in the perturbation V_P . Only the exchange term V_c is considered here. The following expression is used (Slater 1951, Shinohara 1952) :

$$V_c = -3 \left[\left(\frac{3\rho_c}{8\pi} \right)^{1/3} - \left(\frac{3\rho_{0c}}{8\pi} \right)^{1/3} \right], \quad . \quad . \quad . \quad (31)$$

where ρ_{0c} and ρ_c are the densities of the conduction electrons in the pure metal and the alloy, and $-3(3\rho_{0c}/8\pi)^{1/3}$ is the average exchange energy in a gas of free electrons of density ρ_{0c} . The assumptions made are therefore of an ordinary Thomas–Fermi type ; they are probably valid only for parabolic conduction bands with an effective mass μ unity.

The coulombian part $V_c = V_P - V_e$ of the perturbation verifies Poisson's equation (11) and the boundary conditions

$$\begin{aligned} V_c &\rightarrow -Zr^{-1} \text{ for } r \rightarrow 0 \\ V_c(R) &= 0 \end{aligned} \quad (32)$$

with $dV_P/dr=0$ at $r=R$. Keeping in (31) only terms of the first order in $\rho_c - \rho_{0c} \simeq n_0(E_M)(\Delta E_M - V_P)$, the coulombian part V_c and the displacement ΔE_M of the Fermi level obtained have the same form (19) as before if the screening constant q is replaced by q' where

$$q' = q/(1 - 3\mu/2\pi k_M)^{1/2} \quad (33)$$

(k_M is the maximum momentum in the conduction band). The total perturbation V_P would still be given by (19) if, in (19) and in ΔE_M , Z was replaced by

$$Z' = Zq'^2/q^2. \quad (34)$$

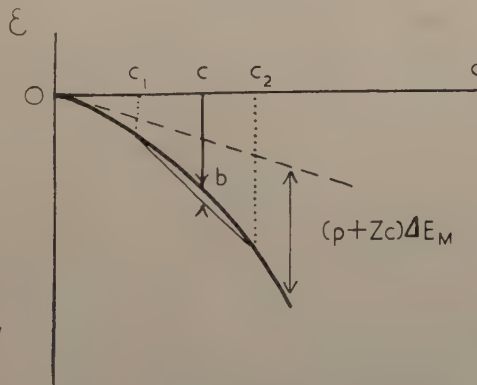
The screening is somewhat more concentrated than that computed previously: for copper, $q'/q=1.7$ for $\mu=1$.

3.7.4. Energies of Solution at Large Concentrations

At larger concentrations, the interaction between solute atoms shifts the conduction band as a whole by ΔE_M (cf. § 3.5); this adds to the energy ϵ an extra term $(p+Zc)\Delta E_M$, where there are p conduction electrons per atom in the matrix (fig. 11). The energy of solution ϵ_A is therefore altered by an amount

$$\delta\epsilon_A = \partial[(p+Zc)\Delta E_M]/\partial c = Z\Delta E_M + (p+Zc)\partial\Delta E_M/\partial c.$$

Fig. 11



ϵ with negative curvature for $Z < 0$.

A straightforward computation using (19) shows that the first term is negligible and gives *

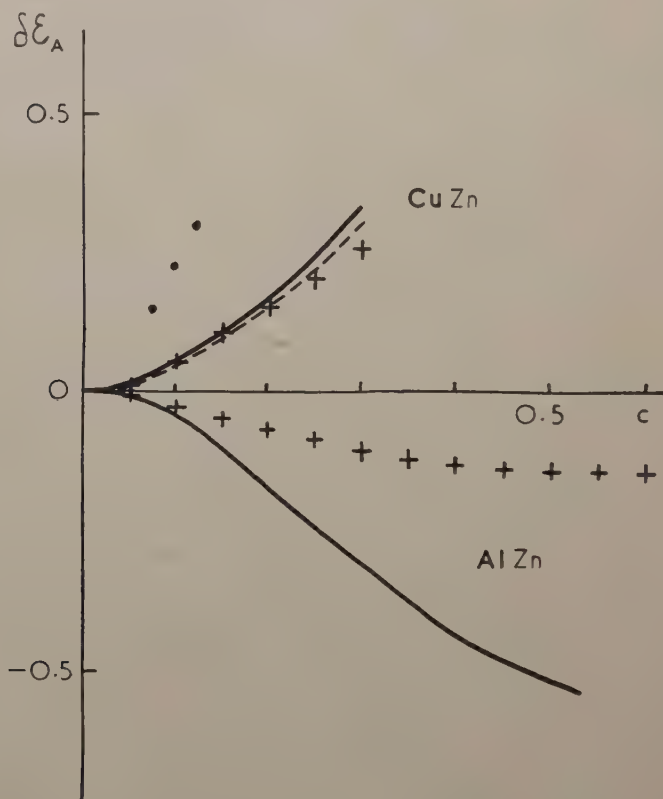
$$\delta\epsilon_A \simeq \frac{2(p+Zc)Zq'^3R^2}{3c(q'R-1)^2 \exp(q'R)}. \quad (35)$$

* Z' was mistakenly used for Z in ΔE_M by Friedel (1954 c) and the values found for $\delta\epsilon_A$ too large by a factor $(q'/q)^2$.

The approximation neglects the *change* in the interaction between V_P and the screening charge; this is easily shown to be negligible.

Figure 12 compares this formula with experimental data for **Cu Zn** ($Z=1$: Herbenar, Siebert and Duffendack 1950) and **Al Zn** ($Z=-1$: Hilliard, Averbach and Cohen 1954). The measurements have been made for values of c greater than 0.05 only; the experimental curves may therefore be shifted parallel to the energy axis so as to match the computed curves at $c=0.05$.

Fig. 12



Change in the energies of solution with concentration for **Cu Zn** and **Al Zn** (in eV/at). Continuous line: eqn. (34); dotted line: correction for size effect; crosses: experimental values; points: displacement of the optical absorption edge in **Cu Zn** (Lowery, Wilkinson and Smare 1937).

The agreement for **Cu Zn** is almost too good, especially with a small correction for the size effect. This effect may be neglected in **Al Zn**; the large discrepancy between computed and experimental values in this case may be due to an especially concentrated screening round the Zn atoms, which belong to a more 'electro-positive' period than Al. Equation (35) assumes also that the solute atoms repel each other (cf. fig. 3), a better approximation for **Cu Zn** than **Al Zn**, as emphasized below.

The following table compares with theoretical values (q' with and q without exchange, and $\mu=1$) the values q_{exp} of the screening constant which give the best fit with the experimental curves $\epsilon(c)$. Values recently measured for solid **Ag** Cd and liquid **In** Ag, **Sn** Ag (Kleppa 1954) are also included. The small correction for elastic energy has not been taken into account.

| | q | q' | q_{exp} |
|--------------|------|------|------------------|
| Cu Zn | 0.96 | 1.64 | 1.65 |
| Ag Cd | 0.90 | 1.78 | 1.8 |
| Al Zn | 1.09 | 1.55 | 1.7 ₅ |
| In Ag | 1.02 | 1.59 | 1.7 ₅ |
| Sn Ag | 1.05 | 1.57 | 1.7 |

The agreement of q_{exp} with the value q' computed with exchange is satisfactory.

3.7.5. Interaction between Solute Atoms

Equation (35) may be used to show that if the effects of polarization and size are less important than the valence difference, the solute atoms are expected to attract each other for $Z < 0$, to repel for $Z > 0$. Experimental data on this point are reviewed.

It is well known that in a solid solution with only *short range* interactions the atoms of one kind attract or repel each other, depending on the sign of the curvature of the energy $\epsilon(c)$ of formation of the alloy defined for dispersed atoms.*

With a negative curvature for instance (fig. 11), a phase with concentration c tends to split at low temperature into two phases with the same structure but different concentrations c_1, c_2 : the solute atoms *attract* each other so as to reduce the energy of the alloy by the amount ab . At higher temperatures, this attraction is compensated by the entropy effect which tends to disperse the solute atoms. A detailed thermodynamical study would require more complex distributions of solute atoms than that of fig. 3. But it may be predicted qualitatively that for each concentration there is a temperature above which there is only one phase with some remaining local ordering: the solute atoms tend still to aggregate in slightly richer zones. Finally a phase with a different crystal structure is often more stable at high concentrations c_2 . It may then be expected that, by quenching and ageing of the solid solution, zones of higher concentrations are formed in the solution in a transitory stage before

* The specific heats must also be additive (Kopp-Neumann rule).

precipitation of the more stable phase. The initial stage of the Guinier-Preston zones has been explained in this way (cf. Meyering 1952).

Conversely, with a positive curvature of $\epsilon(c)$, the solute atoms are expected to *repel* each other. At low temperature, there is no splitting into two phases with the same structure; other phases more stable at higher concentration generally nucleate without prior local enrichment of the solid solution.

In the 'quasichemical' theory usually applied to alloys (cf. Hilliard, Averbach and Cohen *loc. cit.*), one assumes nearest neighbour interactions and the curvature of $\epsilon(c)$ is then related to its slope: at high temperatures where the solid solution is practically random, and if pure solute and solvent have the same crystal structure, this gives $\epsilon \propto c(1-c)$, thus $d^2\epsilon/dc^2 = -2(d\epsilon/dc)_0$. Thus like atoms would attract each other in an exothermic alloy ($d\epsilon/dc > 0$), repel in an endothermic one (cf. Wagner 1952, Lumsden 1952; also Yvon 1945, Fournet 1953 for more elaborate theories).

No relation of this kind exists in the present computation; fig. 11 shows on the other hand that $\epsilon(c)$ has the same curvature as $(p+Zc)\Delta E_M$ and thus as ΔE_M at not too large concentrations. Figure 5 shows that ΔE_M has the sign of Z : whatever the band structure of the solvent, solute elements repel or attract, depending whether Z is positive or negative.

This analysis does not apply when the *size* factor is preponderant, because elastic interactions are long range ones, and enriched zones cannot be treated independently from the matrix they would deform. It will be shown in the Appendix that ϵ has then a negative curvature but that like atoms probably repel each other, at least at large concentrations. When the *valence* factor is preponderant, the predictions made above seem to agree on the whole with experiment. The following facts may be recalled:

1. The energy ϵ of formation of the alloy has a curvature with the same sign as Z : the curvature and Z are positive in **Cu Zn** (Herbenar *et al. loc. cit.*), **Cu Al** (Oelsen and Middel 1937), **Ag Zn**, **Ag Cd**, **Ag In** (Birchenall and Cheng 1949, Kleppa 1954), **Au Cd** (Kubaschewski and Evans 1951); the curvature and Z are negative in **Al Zn** (Hilliard *et al. loc. cit.*), **Pb Tl** (Kubaschewski and Evans 1951), **In Ag**, **Sn Ag** (Kleppa 1954), and perhaps **Al Cu** (cf. Meyering *loc. cit.*). The only exceptions known to the author are **Au Ni** (Averbach, Flinn and Cohen 1954) and **Cu Pt** (Kubaschewski and Evans 1951) where the curvature has the same sign at both ends of the diagram, being negative for **Au Ni**, positive for **Cu Pt**. A polarization of the d shells may play a role (cf. § 5); the curvature in **Au Ni** is more probably due to the size effect (Averbach *et al. loc. cit.*).

2. In solid solution, the solute atoms attract each other when $Z < 0$: this is shown by x-ray diffuse scattering in **Al Zn** (Rudman, Flinn and Averbach 1953), **Al Ag** (Walker, Blin and Guinier 1952); they repel each other when $Z > 0$: this gives an anomaly of the specific heat in **Cu Zn** (Masumoto, Saito and Sugihara 1952); it explains probably why the

wiping out by quadrupole effect of some nuclear magnetic resonance lines in **Cu** Al occurs on the Cu atoms much more rapidly than on the Al ones with increasing Al concentration (Knight 1953). It is also known that carbon atoms repel each other in iron (Richardson and Dennis 1953); but this effect, as well as the repulsion of like atoms in Au Ni (Flinn, Averbach and Cohen 1953) is perhaps due mainly to the size effect (cf. Appendix).

3. Two face-centred cubic phases co-exist in **Al** Zn at low temperature ($Z < 0$). This is effectively due to a curvature of the energy of formation of the alloy (cf. Averbach *et al. loc. cit.*), not to an anomaly in the entropy as suggested by Leigh (1951). The non-existence of such a phase in **Cu** Ni is perhaps due to some interaction between d shells.

4. Guinier Preston zones form for **Al** Cu, **Al** Ag, **Al** Zn, **Al** Mg, **Al** Mg Cu, **Cu** Ni Co ($Z < 0$), not for **Al** Si, **Mg** Pb ($Z > 0$) (Guinier 1952); zones in **Cu** Be ($Z = 1$) are probably formed by a different mechanism, for their atomic structure is not related to that of the matrix.

5. The solubility of hydrogen ($Z = 1$) decreases in an alloy when the concentration of the elements with higher valency increases * (**Pd** Ag: Cohen 1933; **Al** Si liquid: Niessen 1939; liquid copper alloys: Himmler 1950; solid silver alloys: Schwab 1946). The same is true for interstitial carbon ($Z = 4$) in solutions of elements like Ni, Co in iron (Barrett 1953).

6. Finally special mention should be made of alloys of transition elements. It was predicted in § 3.3. that the solute elements interact weakly, and only above a certain concentration. Effectively in **Fe**_γ Ni ($Z = 2$), the Ni atoms repel slightly for $c > 0.15$ (Oriani 1953). In **Fe**_α Cr ($Z = -2$) with more than 15% Cr, the Cr atoms cluster after prolonged annealing at 470°C; the enriched zones may contain up to 80% Cr (Fisher, Dulis and Carroll 1953); the alloy becomes brittle (Houdremont 1935) and an anomaly in the specific heat appears (Masumoto, Saito and Sugihara 1953).

3.7.6. Displacement of the Optical Absorption Edge in Alloys

The positive hole created by optical or x-ray absorption in an inner atomic shell may jump from atom to atom. But this displacement is very slow: its 'effective mass' is very large because it belongs to a narrow band. The adiabatic approximation is therefore applicable (cf. Seitz 1940): the positive hole may be treated as a *fixed impurity* with $Z = 1$; the conduction electrons must be in equilibrium in its field at the end of the transition, and provide in particular a screening around its charge (Skinner 1932, 1933, Friedel 1952 a, cf. § 5).

In the lowest excited state, no electron is ejected from the metal, and energy is required only to introduce into the metal this special kind of impurity with $Z = 1$. In alloys like **Cu** Zn, this energy must increase with

* Wagner's explanation of this fact is similar, but he considers only the displacement of the Fermi level *relative* to the band structure (cf. Himmler 1950).

zinc concentration: the energy of the Cu absorption edge must change in the same way as the energy ϵ_{Zn} of dissolution of the solute element.

This change is too small to be observed in x-ray transitions, and Cu K_β is effectively unaltered by an increase in Zn content (Bearden and Friedman 1940). The optical absorption peak of noble metals in the visible range has on the other hand been interpreted as due to the creation of d holes (cf. § 5). The absorption edge in Cu Zn should therefore be displaced in the same direction as ϵ_{Zn} , but by a larger amount, because the d hole is probably more diffuse than a point charge,* and its screening extends over a larger distance. One would also expect an edge broader than for pure copper, because copper atoms at various distances from zinc atoms would require different energies to be excited. These points are in agreement with experiment (cf. Lowery, Wilkinson and Smare 1937); fig. 12 compares $\delta\epsilon_{\text{Zn}}$ with the average displacement of the absorption edge. The displacement seems to go to zero at a finite concentration, as is to be expected.

3.8. The Born Approximation. Electrical Properties

The study of electrical properties requires some knowledge of the perturbed wave functions. When the conduction band of the pure metal may be treated as a gas of *free electrons*, the first order approximation of § 3.1 is the classical Born one. This is easily seen by use of an exact relation between the screening charge and the phase shifts of the wave functions for a spherically symmetrical perturbation.

3.8.1. Relation between Screening and Phase Shifts

A gas of free electrons is enclosed in a spherical box with large radius R . The field of potential is assumed to be infinite at the surface of the box and zero inside, except in a limited region $r < R_1$ at its centre where it takes some value $V_P(r)$ with spherical symmetry (fig. 13).

The quantized states have then the form $\phi_l(k, r)P_l(\cos \theta)$, where P_l is the l th Legendre polynomial and θ the angle of \mathbf{r} with the 'momentum' \mathbf{k} ($k = \sqrt{2\mu E}$) of the incoming electron (Mott and Massey 1949). The spherical components $\phi_l(k, r)$ are easily seen to take the asymptotic form $\text{const } R^{-1} \sin(kR - \frac{1}{2}l\pi + \eta_l)$ for $kR \gg \frac{1}{2}l\pi$. The constant 'phase shift' η_l vanishes for $V_P = 0$.

The quantized momenta k are fixed by $\phi_l(k, R) = 0$; as R tends to infinity, this is, with λ an integer,

$$k \simeq R^{-1}[\frac{1}{2}l\pi + \lambda\pi - \eta_l(k)]. \quad . \quad . \quad . \quad . \quad (36)$$

The following may be deduced from this relation:

1. The number of states of quantum number l introduced by the perturbation between two fixed values k_1, k_2 of k is

$$[\lambda_1 - \eta_l(k_1)/\pi] - \lambda_1 - [\lambda_2 - \eta_l(k_2)/\pi] - \lambda_2 = [\eta_l(k_2) - \eta_l(k_1)]/\pi.$$

* Cu⁺⁺3d⁹ is less attractive than Zn⁺⁺3d¹⁰.

The total charge introduced into the gas is, by summation over states l and spins σ ,

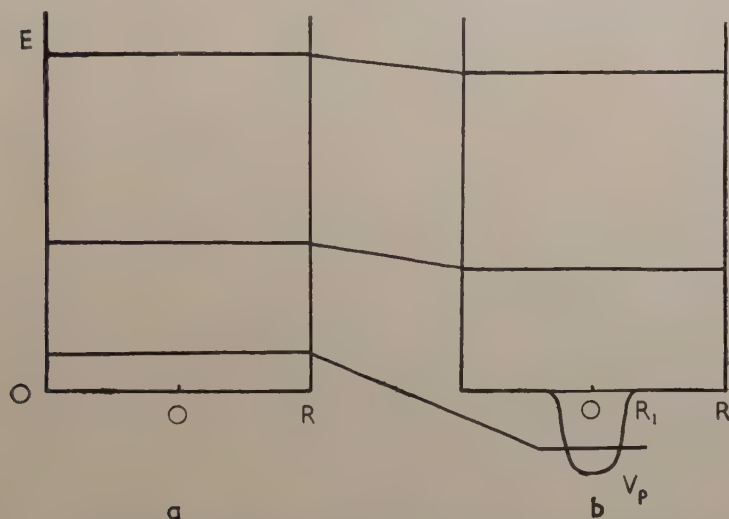
$$\frac{1}{\pi} \sum_{\sigma} \sum_l (2l+1) [\eta_l(k_2) - \eta_l(k_1)].$$

2. It is seen by counting the number of nodes of ϕ_l (cf. Mott and Massey 1949) that if V_P accepts n_l bound l states of negative energy,

$$\eta_l(0) = n_l \pi.$$

The total charge introduced into the gas by V_P below a fixed energy $E = k^2/2\mu$ (bound states included) is therefore

Fig. 13



Displacement of s states quantized in a spherical box.

$$n = \frac{1}{\pi} \sum_{\sigma} \sum_l (2l+1) \eta_l(k). \quad (37)$$

3. The density of charge below E is unaltered at large distances from a localized perturbation V_P (cf. § 2.2.2). The charge n introduced is therefore *localized* in the region where V_P differs from zero or within a distance $R_1' - R_1 \approx k^{-1}$ from that region. n is the charge 'locally displaced' in the gas below energy E .

3.8.2. The Born Approximation

In the Born approximation, a perturbing potential $V_P(r)$ produces, at a distance r , for an l state with energy $k^2/2\mu$ a phase shift

$$\eta_l(k, r) = -\pi \mu \int_0^r V_P(r') J_{l+1/2}^2(kr') r' dr'. \quad (38)$$

J is a Bessel function (cf. Mott and Massey). We show here with the use of (37) that this relation is equivalent to the first order approximation of § 3.1. The charge displaced between 0 and r and below k is

$$Z_0(k, r) = -\mu \sum_{\sigma} \sum_l (2l+1) \int_0^r V_P(r') J_{l+1/2}^2(kr') r' dr'.$$

Using the relation

$$\frac{\sin Kr}{Kr} = \sum_l (2l+1) \frac{\pi}{2kr} \{J_{l+1/2}(kr)\}^2 P_l(\cos \theta), \quad (39)$$

with $K = 2k \sin \frac{1}{2}\theta$ (Watson 1922), eqn. (20) of § 3.1 is effectively obtained.*

3.8.3. Electrical Resistivity due to Impurities

When the conduction electrons may be treated as free in the pure metal, the increase of electrical resistivity due to a concentration c of impurity centres is (cf. Mott and Massey 1949)

$$\Delta\rho = k_M A c / N(E_M),$$

with

$$A = \int_0^\pi (1 - \cos \theta) |f(\theta)|^2 2\pi \sin \theta d\theta$$

and

$$f(\theta) = (2\pi i k_M)^{-1} \sum_l (2l+1) [\exp(2i\eta_l) - 1] P_l(\cos \theta). \quad (40)$$

The impurity centres are assumed here to scatter independently. This treatment is based on Tibbs' approximation (§ 2.1.3) and is therefore good for metals where the centre of the conduction band has s-symmetry and an effective mass μ unity.

The Born approximation replaces $\exp(2i\eta_l) - 1$ by $2i\eta_l$. Equations (38), (39), and (40) then give

$$f(\theta) = 2 \int_0^R \frac{\sin Kr}{Kr} V_P r^2 dr, \quad (41)$$

if the potential V_P of an impurity vanishes for $r \geq R$. The use of (19) for V_P gives

$$f(\theta) = -\frac{2Zq^2}{K^2(q^2 + K^2)} \left[1 + \frac{qR(KR \cos KR - \sin KR)}{KR(qR \cosh qR - \sinh qR)} \right]. \quad (42)$$

At infinite dilutions (R infinite), the bracketed term is unity and (40) gives (Mott 1936)

$$\Delta\rho = \frac{9\pi^2 Z^2 c}{2r_s^3 k_M^6} \left[\ln \left(1 + \frac{1}{y} \right) - \frac{1}{1+y} \right], \quad (43)$$

with $y = q^2/4k_M^2$. The initial slope $\partial\Delta\rho/\partial c$ is therefore proportional to Z^2 , in good agreement with experiment for alloys in noble metals with $Z > 0$

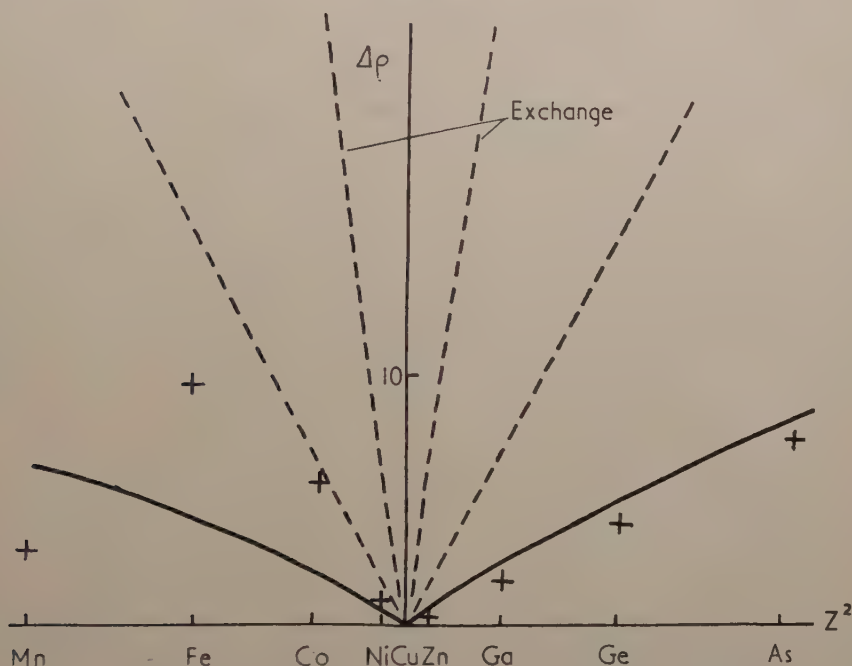
* The change of energy (30) in the gas when V_P is introduced may also be derived directly from the density R/π of l states in k space by the equation

$$\delta E = \sum_{\sigma} \sum_l (2l+1) (R/\pi) \int_0^k k' \cdot \delta k' \cdot dk'$$

with, from (36), $\delta k' = -\eta_l(k')/R$.

(Linde 1939). The computed $\Delta\rho$ are however much too large; the exchange correction of § 3.7.3 increases this discrepancy by a factor 4 for copper alloys (cf. fig. 14). It has been suggested that the behaviour of $\Delta\rho$ for $Z < 0$ is due to the presence of 'quasi bound' states (cf. § 2.1.1) pushed towards the Fermi level by the repulsive perturbation. Such states are known to perturb the phase shifts strongly (Ramsauer-Townsend effect, cf. Mott and Massey 1949). Finally (43) is probably less satisfactory in polyvalent or transitional metals with several bands overlapping at the Fermi level.

Fig. 14



$\Delta\rho$ in $\mu\Omega$ cm for one atomic per cent impurity in copper.

Crosses: experimental points; dotted curves: Mott's approximation, with and without exchange, for $\mu=1$; continuous line: computation of § 4.

At finite concentrations, $\Delta\rho$ should no longer be proportional to c because V_P becomes smaller and the electrons at the Fermi level have their energy shifted by ΔE_M . These two effects reduce $\Delta\rho$ when Z is positive. But this change is very small up to large concentrations, in good agreement with experiment (Linde 1939): the second term in the brackets of (42), due to smaller V_P , is easily seen to be much smaller than $2 \exp(-qR)$, and thus than 2×10^{-3} for copper alloys when $c=0.30$. It is obviously small because, according to (41), $\Delta\rho$ depends mainly on the central part of V_P , which varies little with concentration. The displacement ΔE_M of the Fermi level $E_M = k_M^2/2\mu$ on the other hand changes $\Delta\rho$, according to (43), by a fraction $-2\Delta E_M/E_M$; for Cu Zn with 30% Zn, this is 0.7% with exchange, 5% without.

3.8.4. Thermoelectric Power

At a temperature, not too high but above the Debye temperature the thermoelectric power S of a metal or alloy is given by (Mott and Jones 1936)

$$S = \frac{1}{3} \pi^2 k^{*2} T [\partial \ln \rho / \partial E]_{E_M}. \quad (44)$$

k^* is the Boltzmann constant, $\rho(E)$ the resistivity for a Fermi level E , the actual value of the Fermi level being E_M .

At low concentrations c , E_M is the same in the metal and the alloy, and the relative variation of S by alloying is, according to (44) (cf. Friedel 1953)

$$\frac{\Delta S}{S_0} = \left(1 - \frac{\Delta x}{x_0}\right) / \left(1 + \frac{\rho_0}{\Delta \rho}\right). \quad (45)$$

ρ_0 , S_0 refer to the pure metal; $x_0 = -E_M (\partial \ln \rho_0 / \partial E)_{E_M}$ and

$$\Delta x = -E_M (\partial \ln \Delta \rho / \partial E)_{E_M}.$$

For simple metals and not too large concentrations, $\Delta \rho$ was seen above to be proportional to c ; Δx is therefore a *constant*. As $\Delta \rho / \rho_0 c$ is large in usual metals, $\Delta S(c)$ should, according to (45), be strongly *concave* towards positive c and tend for large c to a constant value $[(\Delta x / x_0) - 1] S_0$. A strong curvature of the right sign is generally observed in alloys of noble metals. The following table shows that the corresponding Δx is nearly constant while ΔS (in $\mu\text{V}/\text{deg.}$) is far from proportional to c :

(a) Cu Fe :

(b) Cu Zn :

| 100c | $\Delta S/100c$ | Δx | | 100c | $\Delta S/100c$ | Δx |
|-------------------|-----------------|------------|--|------|-----------------|------------------|
| 0.03 | -73 | 14.0 | | 4.0 | -0.22 | 0.7 |
| 0.07 ₅ | -60 | 15.0 | | 7.5 | -0.16 | 0.9 |
| 0.10 | -52 | 14.0 | | 11.5 | -0.13 | 0.9 ₅ |
| 0.30 | -21 | 11.5 | | 15.0 | -0.11 | 0.9 ₅ |
| 0.87 | -12 | 14.0 | | | | |

Values of ΔS in this table and the following table are taken from Landolt and Börnstein (1931).†

The value of Δx deduced from Mott's formula (45) for $\Delta \rho$ is

$$\Delta x = 3 - \{ (1+y) [(1+y) \ln (1+1/y) - 1] \}^{-1}, \quad (46)$$

thus a function only of $y = q^2 / 4k_M^2$, not of Z . It decreases from 3 to 1 when y increases from 0 to infinity. For noble metals, (46) gives $\Delta x \simeq 1$ to 2. This is the order of magnitude observed in a number of alloys of *polyvalent*

† Formula (44) with a Δx independent of concentration is valid for any limited perturbation introduced into the metal. It has recently been checked by Druyvesteyn (1954) for dislocations in cold-worked copper.

elements in copper and gold ($Z > 0$), as is shown in the next table. Numbers between brackets come from one measurement only:

(a) $Z \geq 0$

(b) $Z < 0$

| M | Cu M | Au M | | M | Cu M | Au M |
|----|------------|---------|--|----|-------|--------|
| Al | 0.4 to 1.0 | — | | Ti | — | (-3) |
| Cu | — | (-0.25) | | Cr | — | (6.7) |
| Zn | 0.85 | (0.5) | | Mn | -0.35 | (-0.3) |
| As | 2.0 | — | | Fe | 14 | 7 |
| Ag | 0.5 | 1.0 | | Co | 44 | 42 |
| Cd | — | (0.9) | | Ni | 16 | 55 |
| Sn | 1.6 | — | | Pd | 3.5 | (8.4) |
| | | | | Pt | — | 8 |

This good agreement comes perhaps from the fact that it is only the relative variation of $\Delta\rho$ which matters in Δx .

For $Z < 0$, the thermoelectric power is as irregular as the resistivity. In polyvalent and transitional metals with overlapping bands at the Fermi level, ΔS seems mainly due to changes in the number of carriers in the various bands (Mott and Jones 1936, Galt 1949, Wilson 1953, Friedel 1953).

§ 4. MOLECULAR ORBITALS. BETTER APPROXIMATIONS

In eqn. (14), the density $\rho_0(E_M + \Delta E_M - V_P, \mathbf{r})$ was replaced by a development of the first order $\rho_0(E_M) + (\Delta E_M - V_P)\partial\rho_0/\partial E_M$. This approximation is improved in the present section. Corrections to the form of the screening, to the displacement of the Fermi level and to the density of states are introduced by taking into account terms of the second order in $(\Delta E_M - V_P)$; more details are given for parabolic and full bands. Finally the Thomas-Fermi approximation of eqn. (13) itself may be checked in the case of free electrons.

4.1. Second Order Approximation

It is shown in this section that the amount of charge displaced depends on whether the perturbation is attractive or repulsive. Corrections to the picture of rigid bands and an approximate form for V_P are developed.

4.1.1. Charge Locally Displaced. Fe Alloys

If $\rho_0(E - V_P) - \rho_0(E)$ is developed up to terms of the second order in V_P and $\partial\rho_0/\partial E$ replaced as in § 3.1 by $n_0(E)$, the charge locally displaced in the metal by V_P between 0 and r and below energy E is

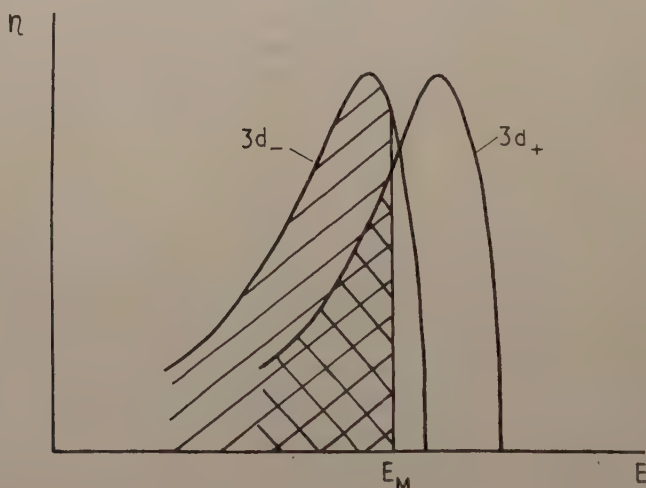
$$Z_0(r, E) = -4\pi n_0(E) \int_0^r V_P r^2 dr + 2\pi(\partial n_0/\partial E) \int_0^r V_P^2 r^2 dr. \quad (47)$$

The additional term in V_P^2 shows that in a band structure with positive slope $\partial n_0/\partial E$ at the energy E , the electrons are more strongly displaced by an attractive than by a repulsive perturbation V_P ; and conversely for $\partial n_0/\partial E < 0$. A gas of free electrons is an example of the first case; a gas of free 'positive holes', one of the latter.

It may also be said that a negative perturbation V_P (due for instance to an impurity with $Z > 0$) attracts the electrons of an almost empty band ($\partial n_0/\partial E_M > 0$) more strongly than it repels the positive holes of an almost full band ($\partial n_0/\partial E_M < 0$); and conversely for $V_P > 0$.

Finally a part of the band structure with definite symmetry properties (a given spin for instance, cf. § 2.1.1) may contribute little to the screening even if the corresponding density of states $n_0(E_M)$ is large, provided the slope $\partial n_0/\partial E_M$ is large and has the right sign, and V_P is strongly localized. In **Fe** Cr alloys for instance, it is perhaps not so much because of its small density n_0 as because of its positive slope $\partial n_0/\partial E$ that the $3d_+$ half band contributes little to the screening of the Cr atoms (fig. 15). This assumes

Fig. 15



Another possible band structure for ferromagnetic iron (cf. fig. 9).

for the 3d band a peak near to its top, in agreement with various computations (Flechster 1952, Fe 3d by tight binding; Krutter and Slater, cf. Seitz 1940, Cu 3d4s by a cellular method). The Fermi level must also be on the left of the peak for $3d_+$ and on the right for $3d_-$, a not unreasonable assumption for ferromagnetic iron.

4.1.2. Density of States

The term in V_P^2 in (47) has the sign to be expected from the approximation of rigid bands of § 2.1.1, but is much larger. This approximation

is actually no longer valid. For the density of states with energy *less than* E in the alloy is

$$\begin{aligned} N(E) &= V^{-1} \int_V \rho_0(E - V_P, \mathbf{r}) d\tau \\ &= N_0(E) - V^{-1} n_0(E) \int_V V_P d\tau + \frac{1}{2} V^{-1} (\partial n_0 / \partial E) \int_V V_P^2 d\tau. \end{aligned}$$

This may be written

$$N(E) = N_0(E - E_0),$$

with

$$E_0 = V^{-1} \int_V V_P d\tau - \frac{\partial n_0}{2n_0 \partial E} \frac{V^{-1} \int_V V_P^2 d\tau - V^{-2} \left| \int_V V_P d\tau \right|^2}{1 - (\partial n_0 / n_0 \partial E) V^{-1} \int_V V_P d\tau} + O_3(V_P). \quad (48)$$

The band structure of the alloy is now deduced from that of the pure metal by a shift E_0 which *varies with* E . The difference from the approximation (23) of rigid bands is a second-order term with the sign of $\partial n_0 / \partial E$, for

$$V^{-1} \int_V V_P^2 d\tau \geq V^{-2} \left| \int_V V_P d\tau \right|^2$$

whatever V_P , and

$$\left| (\partial n_0 / n_0 \partial E) V^{-1} \int_V V_P d\tau \right| \ll 1$$

for the strongly localized perturbations due to impurities at not too large concentrations. (48) is of course no longer valid near the limit of a band, where $\partial n_0 / n_0 \partial E$ becomes infinite.

The band structure of the alloy therefore has not exactly the same form as that of the pure metal. A band presenting a peak with discontinuity in the slope $\partial n_0 / \partial E$ for instance splits by alloying into two separate halves, whatever the sign of V_P . Conversely, alloying makes two *overlapping* bands interpenetrate more (cf. Friedel 1954 c).

The density of states *with energy* E in the alloy is

$$n(E) = dN/dE = n_0(E - E_0)(1 - dE_0/dE).$$

Equation (48) gives, when

$$\begin{aligned} &\left| (\partial n_0 / n_0 \partial E) V^{-1} \int_V V_P d\tau \right| \ll 1, \\ \frac{dE_0}{dE} &= -\frac{1}{2} \left[\frac{\partial}{\partial E} \left(\frac{\partial n_0}{n_0 \partial E} \right) \right] \frac{V^{-1} \int_V V_P^2 d\tau - V^{-2} \left| \int_V V_P d\tau \right|^2}{1 - (\partial n_0 / n_0 \partial E) V^{-1} \int_V V_P d\tau}. \end{aligned}$$

It is therefore *smaller* than the corresponding density of states $n_0(E-E_0)$ in the pure metal in the usual case where

$$x = \frac{\partial}{\partial E} \left(\frac{\partial n_0}{n_0 \partial E} \right) < 0.$$

For a gas of free electrons for instance,* $n_0 \propto E^{1/2}$, thus $x = -(2E^2)^{-1}$; for a gas of free positive holes, $n_0 \propto (E_0 - E)^{1/2}$, thus $x = -[2(E_0 - E)^2]^{-1}$. This reduction in the density of states is related to the fact that, for localized perturbations, bound states may occur between the energy bands and are *subtracted* from these bands (cf. § 2.1.1).

4.1.3. The Perturbing Potential

The self consistent solution for V_P around a charge Z could be obtained by solving numerically Poisson's equation for the boundary conditions (18). In an *approximate* solution, a reasonable form may be taken *a priori* for V_P and the parameters it contains fixed so that the screening charge in a sphere $r \leq R$ is equal to Z . Thus

$$\begin{aligned} Z &= \int_0^R [\rho(E_M + \Delta E_M, \mathbf{r}) - \rho_0(E_M, \mathbf{r})] 4\pi r^2 dr \\ &= 4\pi n_0(E_M) \int_0^R (\Delta E_M - V_P) r^2 dr + 2\pi \frac{\partial n_0}{\partial E_M} \int_0^R (\Delta E_M - V_P)^2 r^2 dr \\ &\quad + O_3(\Delta E_M - V_P). \quad \dots \quad (49) \end{aligned}$$

Taking for V_P the same form (19) as before, but with q_1 now a parameter :

$$V_P = \Delta E_M - \frac{Z}{r} \frac{q_1 R \cosh q_1(R-r) - \sinh q_1(R-r)}{q_1 R \cosh q_1 R - \sinh q_1 R}, \quad (50)$$

with

$$\Delta E_M = Z q_1 / (q_1 R \cosh q_1 R - \sinh q_1 R),$$

(49) gives

$$Z = 4\pi n_0(E_M) Z / q_1^2 + 2\pi (\partial n_0 / \partial E_M) Z^2 / 2q_1 + O[\exp(-2q_1 R)], \quad (51)$$

thus, for small Z and not too large concentrations,

$$q_1 \sim q + aZ, \quad \dots \quad (52)$$

where $a = \frac{1}{2} \pi \partial n_0 / \partial E_M$ and $q^2 = 4\pi n_0(E_M)$ as in § 3.

The screening radius q_1^{-1} , and thus the displacement ΔE_M of the Fermi level, vary now with Z and $\partial n_0 / \partial E_M$. The screening is more concentrated in a gas of particles which are *more easily displaced by a given perturbation* (electrons for $Z > 0$, positive holes for $Z < 0$).

4.1.4. The Hume-Rothery Rules

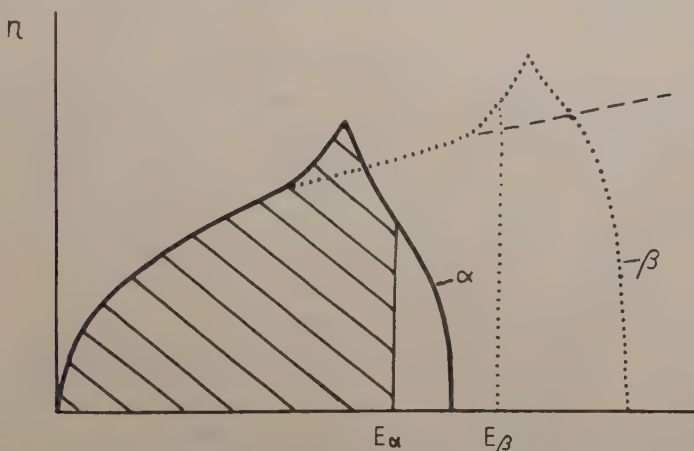
When explaining the Hume-Rothery rules in the approximation of rigid bands, Jones (1934) assumed that the potential energy was independent

* Shinohara (1952) first pointed out this effect for a screened Coulomb field.

of the phase structure. He was able to show by minimizing the kinetic energies that the Fermi levels E_α , E_β of two co-existent phases α , β were in the positions pictured fig. 16: respectively just before and just after the peak occurring when the Fermi surface touches the limits of a Brillouin zone in the metal.

Some difference in V_P , thus in potential energy should however be expected from the very different slopes $\partial n_0/\partial E_M$ of the two bands at the Fermi level. The potential energy may be taken as the sum of the interactions E_1 , E_2 of V_P with the unperturbed conduction band and with the

Fig. 16



Positions of two co-existent phases, according to Jones.

displaced charge

$$E_1 = V^{-1} \int_V V_P d\tau = -V^{-1} Z q_1^{-2}$$

and

$$E_2 = V^{-1} \int_V V_P [d^2(r V_P)/dr^2] r dr = -\frac{1}{2} V^{-1} Z^2 q_1$$

for small concentrations. Relation (52) shows that the difference in E_1 due to $\partial n_0/\partial E_M$ makes the α phase always more stable with respect to the β phase than predicted by Jones; the difference in E_2 makes the α phase more stable for negative Z , less stable for positive Z .

It is therefore expected on that account that, especially for large $|Z|$, the limiting ratios of conduction electrons per lattice site are smaller for $Z > 0$ than for $Z < 0$.

This difference between the limiting electrons per lattice site ratios for positive and negative Z may explain the abnormally high negative

* Figure 16 shows also a small difference in the densities of states at the Fermi level; it is easily seen that the corresponding difference in q , thus in q_1 , would cancel out for small Z the effect described in the text; the difference in concentration stabilizes the β phase (cf. § 3.7.4).

valencies' proposed by Raynor and others (Pratt and Raynor 1951, Robinson 1953, Robinson and Black 1953) for transitional metals in Mg, Al or Si base compounds. These authors suggest that Ni, Co, Fe and perhaps Mn ($Z = -3, -4, -5, -6$) dissolve in Al with their full d shells, and thus subtract 0, 1, 2, 3 electrons per atom respectively from the conduction band of the alloy.* The usual analysis of the Hume-Rothery phases (free conduction electrons with a Fermi sphere near to the limits of a Brillouin zone, cf. Jones 1934) suggests negative valencies larger than 0, -1, -2, -3 for Ni, Co, Fe, Mn (Raynor suggests -0.6, -1.6, -2.6, -3.6; Robinson even larger values). It is equivalent to say that the electron-atom ratios are larger than those observed for positive Z , as was predicted.†

4.2. Parabolic Bands

The displaced charge has been so far replaced by a development in terms of $\partial\rho_0/\partial E_M$ and $\partial^2\rho_0/\partial E_M^2$. The validity of such a procedure may be checked by computing the displaced charge numerically in the simple case of one impurity Z dissolved in a gas of *free electrons* or free positive holes. The Thomas-Fermi type of approximation, $\rho(E, \mathbf{r}) \sim \rho_0(E - V_P, \mathbf{r})$ will at first be retained; later a direct computation is made.

4.2.1. The Perturbing Potential

As in § 4.1.3, the form $V_P = -Zr^{-1} \exp(-q_1 r)$ is assumed and the parameter q_1 fixed so that the screening charge $Z_0(E_M)$ is equal to Z . In the Thomas-Fermi approximation,

$$Z_0(E) = \int_{r_0}^{\infty} \rho_0(E - V_P, \mathbf{r}) 4\pi r^2 dr - \int_0^{\infty} \rho_0(E, \mathbf{r}) 4\pi r^2 dr, \quad (53)$$

with $E - V_P < 0$ for $r < r_0$ and $\rho_0 = k^3/3\pi^2$ ($k^2 = 2\mu E$). This equation shows that $\beta = Z_0 q_1^3/k^3$ is a function only of $\alpha = Zq^2 q_1/k^3$, where $q^2 = 4\mu k/\pi$. The curve $\beta(\alpha)$ is easily drawn with the use of asymptotic values (fig. 17). For small values of α and thus of Z , the second order approximation of § 4.1 gives

$$\beta \simeq \alpha(1 + \pi\alpha/16). \quad (54)$$

As α and thus $Z \rightarrow -\infty$, the screening is mainly due to the band being emptied of its electrons for $r < r_0$, and

$$\beta \simeq -\frac{4}{9\pi} [\ln(-\alpha)]^3. \quad (55)$$

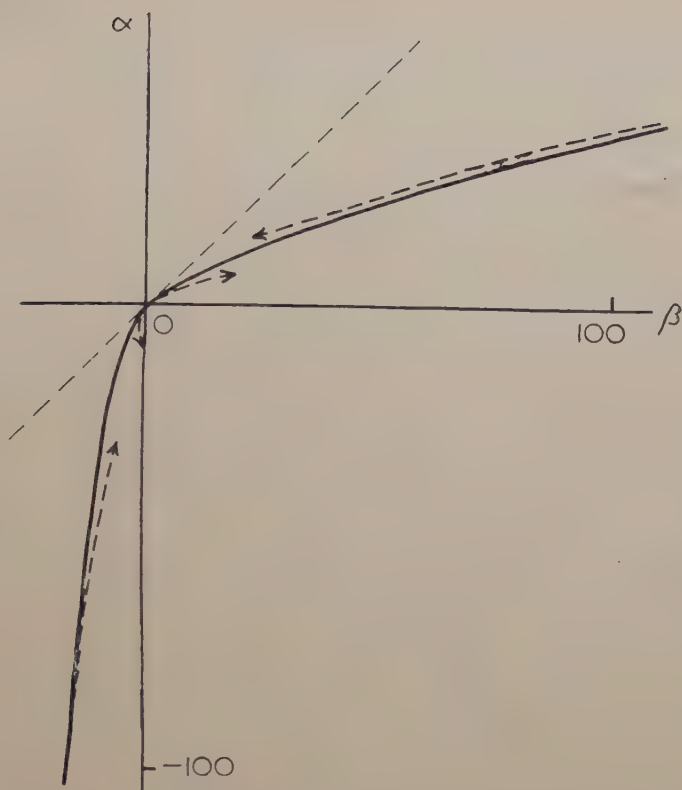
Finally as α and thus $Z \rightarrow +\infty$,

$$\beta \simeq \frac{2\pi}{9\sqrt{3}} \alpha^{3/2}. \quad (56)$$

* The assumption of full d shells in these alloys agree with their weak paramagnetism (Weiss and Klemm 1940, Vogt 1954) and x-rays structure analysis (Taylor 1952).

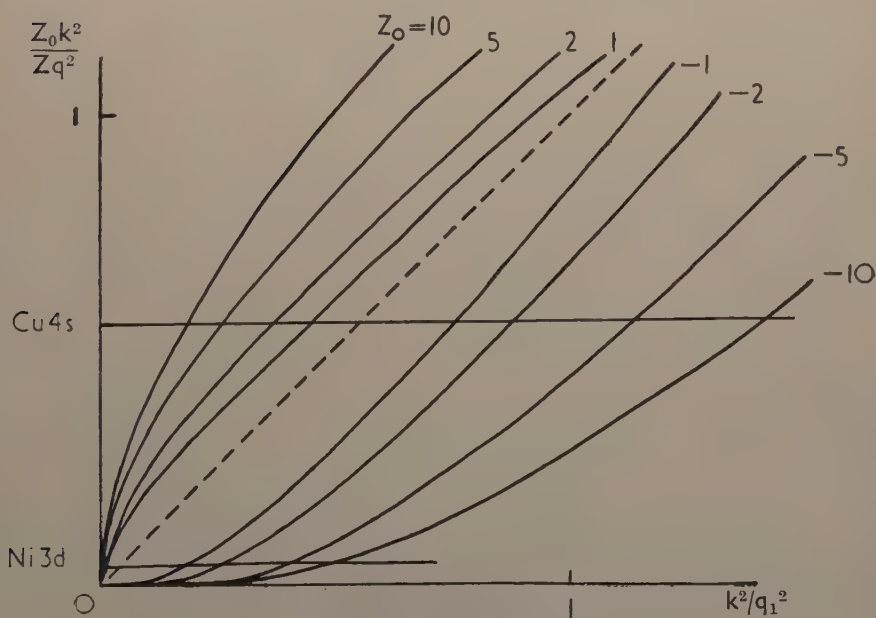
† Raynor's conclusions have however been criticized recently by Hume-Rothery (1954).

Fig. 17



Curve $\beta(\alpha)$. Punctuated lines : asymptotic curves 54, 55, 56.

Fig. 18



Computation of q_1 .

To compute the values of q_1 corresponding to $Z_0(E_M)=Z$, a family of curves $Z_0 k^2/Zq^2$ as functions of k^2/q_1^2 may be drawn for various values of Z_0 (fig. 18). The ordinate is known at the Fermi level of a given metal; the intercept of the horizontal line with the various curves gives the corresponding values of q_1 . In both figures, the dotted straight line corresponds to the first order approximation.

The following points may be deduced from the figures:

1. The screening radius is smaller for * $Z>0$ than $Z<0$; the difference increases with $|Z|$.

2. This agrees with the second order approximation of § 4.1, which is reasonably good for small values of α , thus for our usual metals and small Z . The following table compares the values of q/q_1 obtained for copper (with $\mu=1$) by the two methods.

| $Z \quad q/q_1$ | § 4.1 | § 4.2 |
|-----------------|-------|-------|
| -10 | — | 1.57 |
| -8 | — | 1.53 |
| -6 | — | 1.46 |
| -4 | 2.25 | 1.37 |
| -2 | 1.55 | 1.23 |
| 0 | 1 | 1 |
| 2 | 0.65 | 0.80 |
| 4 | 0.45 | 0.70 |
| 6 | — | 0.63 |
| 8 | — | 0.60 |
| 10 | — | 0.57 |

The differences are due to the curvature of the band and for negative Z to the fact that the method of § 4.1 assumes $r_0=0$ in eqn. (53).

3. For positive holes in the d band of transitional metals like nickel, q^2 , thus α and β are too large for the second order approximation to be valid. Figure 18 shows that the screening is *very broad* for $Z>0$ (**Ni** Cu): *the perturbation cannot repel more positive holes than there are in the d band*; in nickel with 0.6 d holes per atom, the screening must overlap the neighbouring atoms even for $Z=1$. Impurities like H, C, Cu, Zn, Ga dissolved in Ni, Pd, or Pt will therefore interact at rather large distances, and thus for small concentrations, in agreement with experiment (cf. § 3.7.5). For $Z<0$, the screening is conversely very concentrated and impurities like Co, Fe . . . interact little when dissolved in nickel. The d band is however far from parabolic below the Fermi level.

* This is for a gas of electrons. The signs are reversed for a gas of positive holes.

4.2.2. Density of States

For concentrations c small enough for the displacement of the Fermi level to be negligible, the relative variation with c of the density of states at the Fermi level is

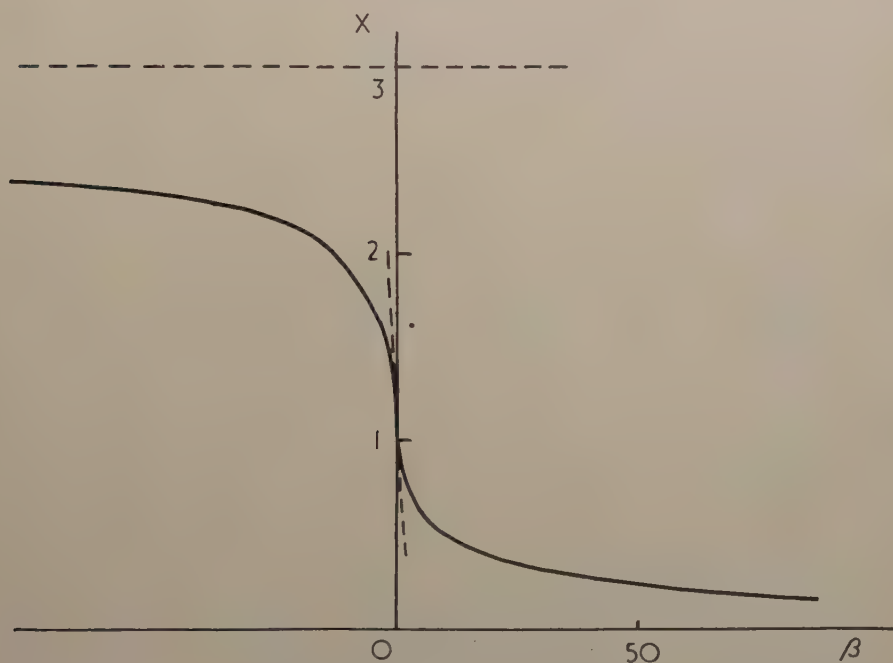
$$\frac{n(E_M) - n_0(E_M)}{n_0(E_M)} = \frac{3c}{4\pi r_s^3 n_0(E_M)} \frac{dZ_0}{dE_M},$$

where Z_0 is given by (53). If the pure metal has p electrons per atom, this may be written in terms of α and β introduced above:

$$\frac{n(E_M) - n_0(E_M)}{n_0(E_M)} = \frac{Zc}{3p} \left(3 - 2 \frac{\alpha d\beta}{\beta d\alpha} \right). \quad (57)$$

Figures 18, 19 show that the factor $X = 3 - 2\alpha d\beta/\beta d\alpha$ is such that the density $n(E_M)$ in the alloy is always *smaller* than that computed with rigid bands (§ 3.5).

Fig. 19



Variation of $X = 3 - 2\alpha d\beta/\beta d\alpha$ with β .
Punctuated line : second order approximation.

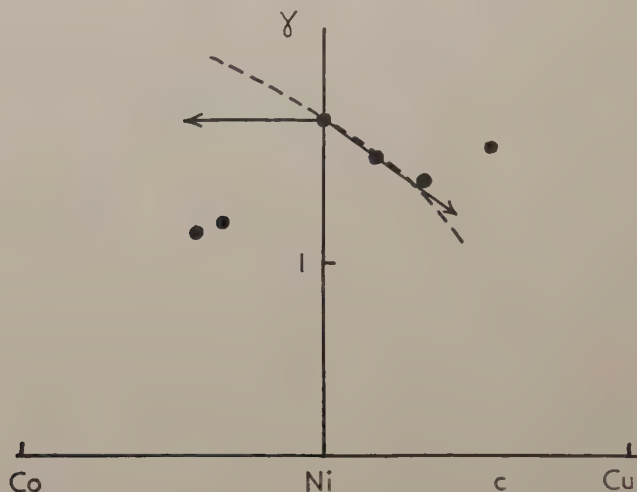
For alloys such as **Cu Zn**, β is small and the second order approximation which sets

$$X = 1 - \frac{\pi q^3 Z}{8 k^3}$$

is not too bad. Large deviations occur in alloys of transitional metals where $|\beta|$ is large. The variation of the low temperature specific heat thus computed for **Ni Cu** is not very different from the first order formula

of § 3.5 ($X=1$), as shown in fig. 20, because of the broad screening in that case. The experimental data are from Keesom and Kurrelmeyer (1940), expressed in 10^{-3} cal/mole deg.². Contributions by 3d and 4s bands have both been taken into account in the computed screening. (57) predicts a horizontal tangent for Ni Fe, but as already pointed out the approximation of a parabolic 3d band is not good in that case.

Fig. 20



Coefficient $\gamma = C_v/T$ in 10^{-3} cal/mole deg.² for **Ni Fe**, **Ni Cu**. Experimental data from Keesom and Kurrelmeyer. Punctuated line: first order approximation (25); arrows: equation (57).

4.2.3. Phase Shifts

The validity of the Thomas-Fermi approximation (53) may be checked by deducing the charge displaced, $Z_0(E)$, from the phase shifts $\eta_l(E)$ through eqn. (37). Improved values of the resistivity due to impurities may also be obtained with these phase shifts.

The phase shifts have been computed numerically for the case $V_P = -Zr^{-1} \exp(-q_1 r)$ (Morse 1932), and curves practically *identical* with those of fig. 18 are obtained (Friedel 1954 c): the Thomas-Fermi approximation is quite satisfactory in this case. The screening radii q_1^{-1} computed for copper alloys are the same within 10% as those given in § 4.2.1.

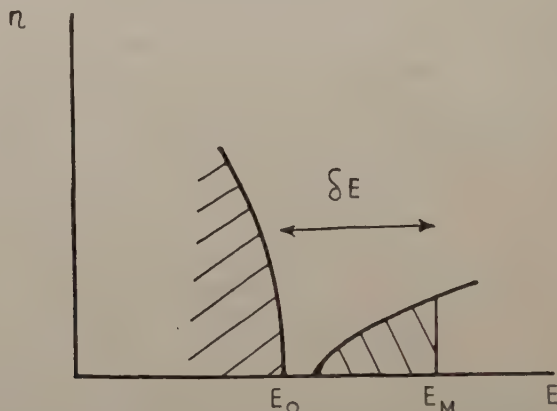
A small concentration c of impurities increases the electrical *resistivity* by an amount which is related exactly to the **p**hase shifts at the Fermi level by the formula (Huang 1948)

$$\Delta\rho = \frac{4\pi c}{k_M^2} \sum_l [(2l+1) \sin^2 \eta_l - 2l \sin \eta_l \sin \eta_{l-1} \cos(\eta_{l-1} - \eta_l)]. \quad \dots \quad (58)$$

it decreases with increasing concentration c , because the bound level widens into a band and also the energy of the Fermi level drops, thus δE decreases by ΔE_M .

In nickel or cobalt-based ferromagnetic alloys, for instance, it is only for small Z and c that the average magnetic moment varies linearly with c with the slope $\alpha = -1$, as predicted in § 3.6. Figure 11 shows that, for large Z and c , the magnetic moment decreases with increasing concentration. This may be due to the full half 3d band of fig. 8 beginning to take

Fig. 21



A full band, below the Fermi level in a metal.

part to the screening. The figure shows, as expected, that for a given solvent the concentration of the band decreases with increasing $|Z|$ (Ni Fe, Ni Mn); it becomes zero for a value of $-Z$ between 3 and 4 for nickel, 1 and 2 for cobalt; δE is of the order of the Curie temperature and thus very small, and formula (59) gives the limits $-Z = 3.2$ and 2.7 respectively, in satisfactory agreement.* †

In copper, zinc or gallium base alloys, the parameter q has similar values and the 3d band is at an increasing distance δE from the Fermi level. Elements with negative Z must thus dissolve with full d shells up to values of $|Z|$ which should increase from copper to zinc and to gallium.

These solute elements subtract therefore from the conduction band the number of electrons necessary to fill up their 3d shells; they are diamagnetic. Elements which dissolve with an incomplete d shell, on the

* The magnetic moment of Ni_3Mn increases on ordering. Ordering increases the average distance between solute atoms, and thus is expected to displace the opening of the full band towards higher concentrations.

† Complications arising from the mixing by alloying of the conduction and d bands are neglected here. Bound d states should be replaced by 'pseudo-bound' states in the conduction band (§ 2.1.1).

other hand, are paramagnetic and subtract fewer electrons from the conduction band. Hume-Rothery rules and magnetic properties (cf. Vogt 1951, 1954, Coles 1953) indicate effectively that the limiting value of $-Z$ for infinite dilutions is probably between 1 and 2 in Cu, Ag or Au; between 3 and 4 in Zn; and between 6 and 7 in Ga, if it behaves as Al does. As expected, this limit decreases with increasing concentration: cobalt atoms dissolve with full $3d^{10}$ shells in the ζ phase of Zn Co (7% Co), but with $3d^9$ shells in the γ phase (14% Co, cf. Coles 1953).*

§ 5. ATOMIC ORBITALS

This section only treats impurities with positive Z and at infinite dilution. Interstitial impurities are introduced as neutral atoms, *in the same state as if in vacuo* (H in copper); ions are similarly substituted for ions with the same charge (Al^+ for Cu^+ in copper); and the remaining gas of valency electrons of the alloy is assumed to be *only slightly perturbed* as regards its average density and energy by the introduction of the impurity.

The screening charge is therefore treated as moving in a field different from that for the remaining valency electrons; this may be studied separately and is usually well known. This removes the difficulties which arise through the self-interaction and correlation in the screening; and this approximation may give satisfactory values for the density of screening (§ 5.1) and the energy of the alloy (§ 5.2), especially for atoms of large Z dissolved in metals like Cu and Al. The approximation applies also to an atom excited in one of its inner shells by x-rays or otherwise (§ 5.3). Some difficulties arise however from the nonorthogonality of the wave functions (§ 5.4).

5.1. Magnetic Susceptibility of Cu Al

The diamagnetism of this alloy increases rapidly with aluminium concentration (Vogt and Harms 1943). In the approximations of this section, the Cu^+ ions may be said to be replaced by larger and thus by more diamagnetic Al^+ ions.

The susceptibilities of Cu^+ and Al^+ differ approximately by

$$(14.7 - 23.5) \times 10^{-6} = -8.8 \times 10^{-6} \text{ C.G.S.}$$

(Friedel 1952 a). This is much more than the increase in paramagnetic susceptibility of the Fermi electrons described in § 4.2.2. Equation (57) gives for this term $\frac{1}{3}X\chi_{Cu}$ per Al atom added, with $X \sim 0.7$. The paramagnetic susceptibility χ_{Cu} of the Fermi electrons of pure copper may be taken as $3/2$ times the difference between the total susceptibility of the metal and that of the Cu^+ ions;† thus

$$\chi_{Cu} = \frac{3}{2}(-5.3 + 14.7) \times 10^{-6} = 14.1 \times 10^{-6} \text{ C.G.S.}$$

* Jones (1953) studied with atomic orbitals the ionization of d shells for larger $-Z$.

† The factor $3/2$ comes from the use of Landau's formula for the diamagnetism of the conduction electrons, assumed unchanged by alloying.

The paramagnetic contribution is therefore 3.3×10^{-6} C.G.S., and the total computed change of susceptibility $(3.3-8.8)10^{-6} = -5.5 \times 10^{-6}$ C.G.S. per Al atom agrees with the measured value -5.9×10^{-6} C.G.S.

In the simple picture of this section, impurities with odd Z are expected to increase the paramagnetism of the alloy, in contradiction with experiment at least for heavy metals (**Cu** Zn, Endo 1925; **Ag** Sb, Vogt 1954). This point is discussed in § 5.4.

5.2. Energies of Solution

The energy of solution of interstitial atoms is obviously zero if the average energy of the conduction electrons is assumed unchanged by their introduction. When the perturbation of the conduction band is taken into account, a negative value of the right order of magnitude is found for **Cu** H (Friedel 1952 a): -2.0 ev per dissociated H atom dissolved, compared with the experimental value -1.6_5 ev/at (Smithells 1949).

For *substitutional* alloys **B** A with p conduction electrons per atom in B, the dissolution of A may be obtained by the following cycle:

1. Evaporate p times an A atom and ionize it.
2. Substitute the A^{P+} ion for a B^{P+} ion.
3. Recombine the B^{P+} ion with the p free electrons and put the B atom back on the B metal.

Operation 2 requires no work if the average energy of the conduction electrons is assumed to be unperturbed by alloying; the energy of dissolution per atom A is thus

$$\epsilon_A = E_B - E_A + \sum_{i=1}^p (i_B - i_A), \quad . \quad . \quad . \quad (60)$$

where E_A , E_B are the cohesive energies and i_A , i_B the ionization potentials. The following table compares these values in ev per atom, with experiment for alloys in noble metals (Kubaschewski and Evans 1951, Kleppa 1954). The accuracy of $E_B - E_A$ taken from Kubaschewski and Evans, and thus of ϵ_A , is about 0.1 ev per atom. The values of i_A and i_B are taken from Bacher and Goudsmit (1932). The data given for **Au** Hg refer to liquid mercury.

| B A | ϵ_A | σ | $\epsilon_A + \sigma$ | Exp. |
|--------------|--------------|----------|-----------------------|-------|
| Cu Zn | -0.5 | 0.1 | -0.4 | -0.35 |
| Ag Cd | -0.4 | 0.1 | -0.3 | -0.33 |
| In | -2.2 | 0.3 | -1.9 | -0.45 |
| Sn | +0.1 | 0.4 | +0.5 | -0.25 |
| Sb | 0.0 | 0.6 | +0.6 | -0.02 |
| Au Hg | -1.6 | 0.1 | -1.5 | -0.56 |

A small correction σ described in the Appendix for size effect has been added.

This calculation may be said to explain why the energies of solution are *small*: it gives a rough account of their variation with Z (e.g. the stability of **Ag In**). As for **Cu H**, the perturbation of the conduction electrons is expected to give more negative values of ϵ_A ; this effect is perhaps compensated in part by a change in the interaction of the d shells. The treatments of these two terms proposed by the author (1952 c, 1954 c) are however too simplified for their results to be trusted.

5.3. *X-rays and Optical Transitions in Metals*

It was pointed out in § 3.7.6 that when an electron is ejected from a *narrow band*, the large inertia of the positive hole created makes it possible to treat the excited atoms containing it as an ordinary impurity with $Z=1$. The conduction electrons thus provide a screening to this charge, at least in the excited states with lower energies: x-rays transitions are complicated multi-electronic processes. At the absorption edge, no electron is ejected from the metal and the only work done is to introduce an excited atom with its screening. As for ordinary impurities, this is most easily done with the approximation of 'atomic orbitals' of this section. But first some general remarks may be made about excited screenings and transition probabilities.

5.3.1. *Fine Structures*

The screening, whatever its form, may certainly take various more or less excited configurations with different energies and possibly different symmetry properties, just as the electron of an impurity centre in a semi-conductor. Secondary emission *bands* and secondary absorption *edges* should therefore be expected in the immediate neighbourhood of the main edge, *on the short wave lengths side* in both cases, their distance from the main edge being equal to the energy of excitation of the screening. Absorption and emission *lines* could also be observed when a direct transition of the inner electron to the screening is allowed by symmetry rules and when the overlap of the initial and final states is sufficient (transitions with large wave-lengths).

This may explain some fine structures observed in the immediate neighbourhood of the main edge and not explicable as Kronig structures related to the band structure (cf. Friedel 1952 for an interpretation in terms of atomic orbitals). As pointed out by Skinner to the author, Auger transitions should however usually widen somewhat the absorption structures and suppress the emission ones.

5.3.2. *Absorption Coefficient at the Main Edge*

An order of magnitude of the absorption coefficient can be obtained by treating the process as a transition of the inner electron to a *plane wave* at the Fermi level: the ejected electron moves in fact in a screened Coulomb field which somewhat increases its density near the excited atom; for the conduction electrons, on the other hand, the probability that they rearrange themselves so as to screen the field of the positive hole, is less

than unity, and these two effects seem to compensate each other (cf. Friedel 1952 b).

The increase in absorption at a K edge is then easily computed (cf. Heitler 1936):

$$\tau = 4 \cdot 2^{1/2} N \phi_0 (137)^3 \frac{Z_x^5 E^{3/2}}{(h\nu')^4 h\nu} \text{ C.G.S.}$$

The effective nuclear charge acting on the inner electron may be taken as $Z_x = \{(Z - 0.3)^2 - 2E_0\}^{1/2}$ where E_0 is the energy of the bottom of the band. E is the Fermi energy, $h\nu$ that of the absorption edge; E_0 , E and $h\nu$ are expressed in atomic units; N is the number of atoms per cm; $h\nu' = \frac{1}{2}Z_x^2 + E$; $\phi_0 = 8\pi e^4/3m^2c^2$ is the classical Thomson scattering factor. Similar expressions are obtained for L and M absorptions (Friedel 1952 b). The following table shows computed values τ (in cm^{-1}) of the right order of magnitude down to the optical range, except for L_I absorptions and perhaps Mg $L_{II, III}$, where the values between brackets are from Townsend (1953).

| | $\tau \times 10^4$ comp. | $\tau \times 10^4$ exp. |
|------------------|--------------------------|-------------------------|
| Li K | 1.3 | 1.0 |
| Be K | 3.3 | 3.5 |
| Mg L_I | 2.5 | 2 or 0.1? (2?) |
| $L_{II, III}$ | 1.4 | 1.4 (8) |
| Al L_I | 3.6 | 2 or 0.2? |
| $L_{II, III}$ | 2.7 | 3.1 |
| Cu M_I | 1.3 | c. 0.5 |
| $M_{II, III}$ | 1.7 | 1.0 |
| $M_{IV, V}$ | 11.0 | 17.0 |
| Zn $M_{II, III}$ | 0.7 | 1.4 |

References to experimental data may be found in Friedel (1952 b) except for Be (Johnston 1954).

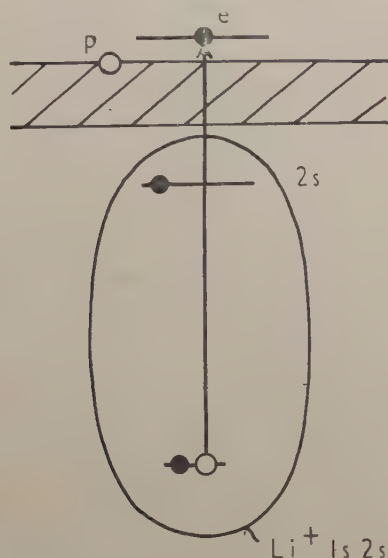
It is of interest to note that if the screening did not take place, the unscreened coulomb field of the positive hole would attract the ejected electron much more strongly, and the absorption would be much stronger; a classical formula due to Stobbe (1930) gives in that case for instance $\tau = 85 \times 10^{-4} \text{ cm}^{-1}$ for the K absorption in lithium.

5.3.3. Absorption and Emission Edges

In the approximation of this section, the K absorption in lithium for instance replaces $\text{Li}^+ 1s^2$ ions by excited $\text{Li}^+ 1s2s$ ones and the average energy of the conduction electrons is assumed to be not much altered by this change. The screening $2s$ electron is produced by the conduction band and a study of the transition probabilities shows that the corresponding positive hole p is at the Fermi level (fig. 22, cf. Friedel 1952 b).

The *absorption edge* corresponds to the case when the ejected electron e just fills in the hole p and the inner hole is at the top of the $1s$ band, and thus at rest. The initial state for the *emission edge* is of course just the same. Energy is only required to excite the inner ion: $\text{Li}^+ 1s^2 \rightarrow 1s 2s$.

Fig. 22



K absorption in lithium.

This is 58.7 eV *in vacuo* (Bacher and Goudsmit 1932), and thus of the right order of magnitude although too large: the observed value is 54.7 eV (Skinner and Johnston 1937). The following table gives similar results in all the other cases where the excitation energy of the inner ion is known experimentally ($h\nu$ in eV, cf. Friedel 1954 c).

| | $h\nu$ ion. | $h\nu$ met. |
|--------------------|------------------|-------------|
| Li K | 58.7 | 54.7 |
| Be K | 118.0 | 111.9 |
| Na } $L_{II, III}$ | 32.7 | 30.5 |
| Mg } $L_{II, III}$ | 52.5 | 49.4 |
| Al } $L_{II, III}$ | 76.4 | 72.5 |
| K } $M_{II, III}$ | 20.0 | 18.5 |
| Ca } $M_{II, III}$ | 25.1 | 24.8 |
| Cu } $M_{IV, V}$ | 2.7 | 2.1 |
| Zn } $M_{IV, V}$ | 9.6 ₅ | 9.5 |
| Ag } $N_{IV, V}$ | 4.8 ₅ | 4.0 |
| Au } $O_{IV, V}$ | 1.8 ₅ | 2.5 |

The discrepancy would be reduced by the same type of correction as for **Cu H** (cf. § 5.2).

The values given for Cu, Ag, Au correspond to the edge of the peak observed in the *optical* absorption, assuming that this is due to an excitation from the d to the s band (Friedel 1952 c). The doublet observed in the K, L and M emissions of these elements has been interpreted as an s-d doublet and has actually an energy of separation of the same order (Bearden and Friedman 1940, Cauchois 1952, 1953, Shinoda, Suzuki and Kato 1954); the s-d doublet of Zn has also been included.

The easy excitation of the d band in noble metals corresponds probably to a strong *correlation* between the d electrons themselves and between d and s electrons. This explains perhaps the difference of 1.5 to 2 eV between the computed and measured cohesive energies of copper (Fuchs 1935, cf. Seitz 1940). Its estimate by the author as a van der Waals energy is not, however, reliable (Friedel 1952 c).

5.4. *Objections to Atomic Orbitals*

Objections based on the Hume-Rothery rules and the magnetic properties of alloys may be raised against the use of atomic orbitals for valency electrons.

5.4.1. *Hume-Rothery Rules*

The difficulty arises from the fact that the electrons in atomic orbitals and the conduction electrons move in different fields of potential. The Hume-Rothery rules, as explained by Jones, assume that the valency electrons of the alloy are all in the same conduction band or, as pointed out in § 2.1.1, in bound states subtracted from it by the perturbation. For these rules to be valid, *the potential acting on the conduction electrons must therefore subtract from the bottom of the conduction band as many bound states as there are electrons in atomic orbitals*. The potential acting on the conduction electrons of copper must for instance subtract one state around a H or Zn atom, two around a Ga atom, etc. . . . This is precisely a condition for the atomic orbitals to be nearly orthogonal to the states in the conduction band, and thus for their use to be valid.

The example of **Cu H** shows how this subtraction occurs (Friedel 1952 a): because of a strong *exchange* attraction, the potential acting on the half conduction band with spin parallel to that of the 1s electron of H is strong enough to subtract a bound state from it; the potential acting on the other half does not contain such an exchange term and does not subtract any bound state; the computed phase shifts of the s components at the bottom of the conduction band are accordingly π and 0 respectively.

There is another case where atomic orbitals are nearly orthogonal to the conduction electrons and may therefore be used: if the impurity keeps more than Z valence electrons in tightly bound states, the resulting coulombian potential may repel the conduction electrons sufficiently for their overlap with the atomic orbitals to be small. The atomic orbitals do

not correspond in that case to bound states subtracted from the conduction band. This approximation is often used to describe *ionic solids* for concentrations such that the conduction band of the metallic element becomes empty. It is probably not valid in metallic solid solutions, the coulombian repulsion being never large enough to offset the attraction due to exchange.

5.4.2. Magnetic Properties

Because of the asymmetry assumed between electrons with opposite spin directions, impurities with *odd* values of Z should show some paramagnetism, in contradiction with experiment, at least in heavy metals (**Cu Zn, Ag Sb**, cf. § 5.1): only bound states with an even number of electrons seem to be subtracted from the band, the remaining screening charge being obtained by an equal heaping up of 'free' conduction electrons with both spins. The use of atomic orbitals to compute the energy may then be justified only as a simple device to evaluate interactions between electrons, in a configuration which is admittedly not the most stable one.

It would be hard to compute whether, in a given alloy with an odd value of Z , an asymmetry between the two spin directions would lower the energy or not. Even the simple case of the H^- ion *in vacuo* is difficult (cf. Chandrasekhar 1944). It is for *light metals excited by X-rays* that such an asymmetry is most probable, because:

1. The higher energy of the conduction electrons makes a screening in the conduction band less favourable than in heavy metals.
2. The energy of the excited ion depends markedly on the spin direction of the screening electron (difference of 1.5 ev for $Li^+ 1s 2s$).

The use of atomic orbitals should, therefore, be most appropriate in that case; it seems effectively to explain some of the fine structures observed in x-rays (Friedel 1952 a).

APPENDIX

THE SIZE FACTOR

The distortions of the lattice due to a difference in 'size' between the components of an alloy have been studied by various authors by the methods of *classical elasticity* (cf. Pines 1941, Seitz 1946, Lawson 1947, 1950, Crussard 1950, Eshelby 1953); the results used in this paper are reviewed in this Appendix. More detailed studies have so far only been attempted in special cases (vacancies and interstitials: Huntington and Seitz 1942, Huntington 1942, 1953, Dexter 1952, Dienes 1952; large concentrations: Varley 1953).

The strain energy will be computed, and its value compared with the energy of solution for substitutional alloys; it disappears at least partly by fusion, and explains quantitatively the limiting value of 'favourable' size factors; finally it is pointed out that the size factor gives rise to only

short range forces of interaction between solute atoms, leading to ordering at high concentrations. The simpler case of infinite dilutions is treated first.

1. Infinite Dilutions

The free energy of distortion computed here is compared with experiment; the variation of the elastic constants with temperature gives rise to a large entropy term; there is no long range interaction between solute atoms.

1.1. Strain Energy

A spherical hole with radius r_s , the radius of the atomic sphere, is cut into the matrix, treated as a continuous, isotropic and elastic medium. A solute atom, represented by a sphere of radius r'_s , is introduced into the hole. At equilibrium, the surface of contact between solute and solvent is a sphere of intermediate radius a .

The strain energy of the matrix is, if χ is its compressibility and ν its Poisson ratio (Timoschenko 1934),

$$E = \frac{12\pi(1-2\nu)}{1+\nu} \frac{r_s(a-r_s)^2}{\chi}.$$

The strain energy of the solute atom is

$$E' = \frac{6\pi r'_s(a-r'_s)^2}{\chi'}.$$

The equilibrium at the surface of contact gives $d(E+E')/da=0$, thus

$$\sigma = E + E' = 6\pi\delta^2 r'_s / (1+\alpha)\chi', \quad . \quad . \quad . \quad (61)$$

with $\alpha = (a-r_s)/(r'_s-a) = (1+\nu)\chi r'_s / 2(1-2\nu)\chi' r'_s = E/E'$, and $\delta = r'_s - r_s$.

The elastic constants of the pure solute and solvent will be used. This is not very satisfactory for the solute atom, which is strongly deformed and in a different electronic state. But the total strain energy does not depend very much on the actual values taken for the solute, for the major part of the energy is usually stored in the matrix; for $\nu \sim \nu' \sim 0.33$ and $\chi' \sim \chi$, $E/E' = \alpha \sim 2$ (Crussard loc. cit.).

1.2. Free Energies of Solution

σ is the work done to introduce a solute atom. The following table shows that, for divalent metals dissolved into each other, it is of the same order of magnitude as the atomic part of the free energy of solution, ΔF_A , obtained by subtracting from the total free energy of solution the part due to the entropy of position. σ and ΔF_A are expressed in ev per atom; the compressibilities are taken from Mott and Jones (1936) and corrected for the temperature T where ΔF_A is measured, assuming that the Poisson ratios ν do not vary with temperature (Köster 1948); ν is taken from Köster (1938) and Landolt and Börstein (1931). ΔF_A was deduced from the limit of solubility c at temperature T by the relation (Cottrell 1948)

$$\Delta F_A = \frac{k^*T}{1-2c} \ln \frac{1-c}{c}. \quad . \quad . \quad . \quad (62)$$

This assumes complete disorder and the atomic part of the free energy of solution varying as $\Delta F_A (1-2c)$. The values thus computed are too large if there is a stable intermetallic compound; this is the case in most of these alloys, and the agreement between σ and ΔF_A may therefore be considered as satisfactory.

| | MgCa | MgZn | ZnMg | ZnCd | ZnHg | CdZn | HgZn |
|------------------------|------|------|------------------|-------------------|-------|-------------------|-------|
| $T^\circ\text{K}$ | 790 | 615 | 615 | 540 | 300 | 540 | 300 |
| $2 \delta /(r_s+r'_s)$ | 0.20 | 0.14 | 0.14 | 0.12 ₅ | 0.14 | 0.12 ₅ | 0.14 |
| α | 1.0 | 1.9 | 1.0 ₅ | 1.2 | 0.7 | 1.9 | 3.1 |
| σ | 0.25 | 0.13 | 0.13 | 0.13 | 0.17 | 0.11 | 0.13 |
| ΔF_A | 0.32 | 0.30 | 0.31 | 0.32 | >0.15 | 0.17 | >0.11 |

The variation with temperature of the elastic constants, thus of σ , corresponds to a large *positive* term in the *entropy* of solution

$$\Delta S = -\frac{\partial \sigma}{\partial T} = \frac{\sigma}{1+\alpha} \left(\frac{\partial \chi'}{\chi' \partial T} + \alpha \frac{\partial \chi}{\chi \partial T} \right) \dots \dots \dots (63)$$

Such a positive anomaly has been observed in various alloys with large size factors (**Zn Cd** and **Cd Zn**: Lumsden *loc. cit.*; **Au Ni**: cf. § 2).

1.3. Interactions between Solute Atoms

The free energy of interaction between two solute atoms is the work done by the stresses due to one of them when the other is introduced. With the spherically symmetrical model used here, the hydrostatic component only can do work, and it is zero, because the matrix has no dilatation. The energy of interaction and its gradient the *force* of interaction are thus zero.

When two solute atoms are in *contact*, the spheres of § 1.1 would interpenetrate. The model is not strictly applicable and there may be an energy of interaction. It is difficult to decide *a priori* whether it is attractive or repulsive. It should, however, be small in close packed metals where the atomic polyhedra are almost spherical. In the **Au Ni** alloys studied in § 3, the interaction between solute atoms seems effectively to be very small at infinite dilutions (cf. Flinn, Averbach and Cohen 1953).

A large number of solute atoms can on the contrary release the major part of their strain energy by forming suitable aggregates. Equation (61) shows that no energy is gained if they cluster into a sphere. The most stable configuration is of course a plate; this allows the stresses to be relaxed across the faces of the plate. The following points may be shown by treating the plate as a flat ellipsoid of revolution (Nabarro 1940, Kröner 1954).

(1) For a given number of solute atoms, the most stable configuration is the *thinnest* possible plate; the plate must be one atom thick, and on the crystallographic plane with lowest density such that the atoms of the matrix on either side of it are not nearest neighbours and can thus relax their stresses. This plane is (100) in both face- and body-centred cubic lattices.

(2) Even such plates must have a large number of solute atoms to relax appreciably their strain energy: about 20 atoms are necessary to decrease the strain energy by $\frac{1}{3}$.

In conclusion, the interactions due to the size factor are probably of a too short range and too weak, compared with the valency factor, to explain the nucleation of the Guinier-Preston zones. But the size factor must affect strongly the form of these clusterings once they are formed. The zones seem indeed to be spherical for very small size factors (**A1** Ag, **A1** Zn) and platelike along a (100) plane for large size factors (**A1** Cu). The fact that the plates are along a definite crystallographic plane strongly suggests that they are one atom thick, at least in their earlier stages.

2. Finite Concentrations

The solution of § 1.1 of the Appendix is no longer valid, because it leads to surface stresses which remain *finite* even when the crystal extends to infinity. These stresses must be compensated by 'image' stresses which produce a supplementary strain in the crystal. If the crystal extends to infinity and if the solute atoms are distributed fairly uniformly (or cluster in zones distributed fairly uniformly), a uniform dilatation e is produced (Eshelby 1954). It must compensate exactly the dilatation $-3(r_s' - a)/r_s'$ of the solute atoms, for the total volume of an elastic medium is unaffected by the introduction of internal stresses. Thus

$$e = 3c(r_s' - a)/r_s' = -3\delta c/(1 + \alpha)r_s'. \quad (64)$$

2.1. Energies and Entropy of Solution

The dilatation e corresponds to a strain energy of interaction of a solute atom with all the others

$$\sigma_i(c) = -4\pi\bar{r}_s^2 \delta e/\chi = -12\pi\bar{r}_s^2 \delta^2 c/(1 + \alpha)\chi, \quad (65)$$

if \bar{r}_s is an average value of r_s and r_s' .

The total strain energy of solution is thus no longer a constant

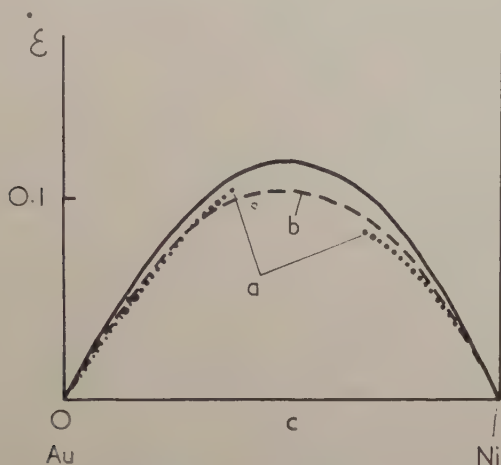
$$\sigma(c) = \sigma(0) + \sigma_i(c) = \frac{6\pi\bar{r}_s^2 \delta^2}{(1 + \alpha)\chi} \left(1 - 2\frac{\chi'}{\chi}c\right). \quad (66)$$

The corresponding term in the free energy of formation of the alloy has a negative curvature

$$\Delta F(c) = \int_0^c \sigma(c) dc = \frac{6\pi\bar{r}_s^2 \delta^2}{(1 + \alpha)\chi} c \left(1 - \frac{\chi'}{\chi}c\right). \quad (67)$$

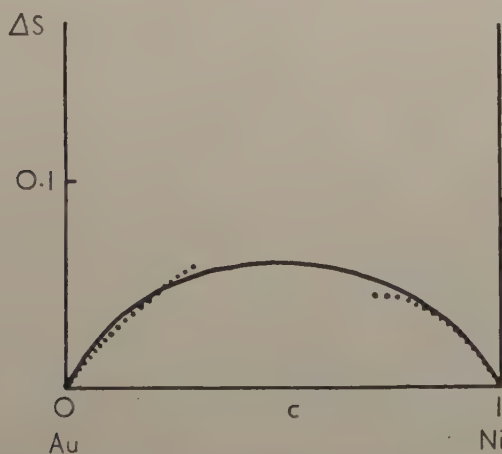
As in § 1 of the Appendix, the strain energies σ and ΔF are the atomic parts of the free energies of solution and of formation of the alloy, from which internal energy and entropy terms may be computed, knowing the variation of the compressibilities with temperature.

Fig. 23



Energy of formation of AuNi alloys (in eV per atom); continuous line : experimental data ; dotted lines : (a) eqn. (67) ; (b) eqn. (68).

Fig. 24



Positive anomaly of the entropy of formation of AuNi alloys (in eV per atom per degree). Continuous line : experimental data ; dotted lines : eqn. (67).

Figures 23 and 24 show that formula (67) explains satisfactorily the energy and entropy of formation of Au Ni alloys at 900°C, both in the gold-rich and the nickel-rich regions. These alloys with a large size factor ($|\delta|/\bar{r}_s = 0.14$) were studied experimentally by Averbach *et al.* (*loc. cit.*).

The internal strain energy of formation is more usually written as

$$\Delta H = \frac{6\pi\bar{r}_s\delta^2}{(1+\bar{\alpha}_0)\bar{\chi}_0} c(1-c) \quad . \quad . \quad . \quad . \quad . \quad (68)$$

where $\bar{\alpha}_0$ and $\bar{\chi}_0$ are average values, taken at room temperature. This assumes that the two components have similar elastic energies and uses the fact that the Young's moduli vary nearly linearly with temperature. Figure 23 shows that, for Au Ni alloys, this is a satisfactory approximation for the whole range of concentrations.

2.2. Limiting Value of the Size Factor

The total free energy of formation of an alloy is, if the size factor is preponderant and if there is total disorder,

$$F \simeq \frac{6\pi\bar{r}_s\delta^2}{(1+\bar{\alpha})\bar{\chi}} c(1-c) - k^*T \{ c \ln c + (1-c) \ln (1-c) \},$$

where \bar{r}_s , α and $\bar{\chi}$ are average values. It is easily seen that, below a critical temperature T_0 , $F(c)$ has two turning points. The phase diagram shows, therefore a miscibility gap below T_0 . T_0 is found to be

$$T_0 = \pi \delta^2 r_s / k^* \chi.$$

The solute and solvent metals have, therefore, a range of *complete miscibility* only if T_0 is lower than the temperature T_s of the solidus, thus for

$$\left| \frac{\delta}{r_s} \right| < \left(\frac{k^* T_s \chi}{\pi r_s^3} \right)^{1/2}.$$

The reasonable value $\chi T_s r_s^{-3} = 10^{14}$ C.G.S. for alloys leads to the condition $|\delta|/r_s < 0.15$, in agreement with Hume-Rothery's experimental rule for substitutional alloys (cf. Jaswon, Henry and Raynor 1951).

2.3. Interactions between Solute Atoms

The part in the dilatation e of the matrix due to one solute atom is vanishingly small. So is, therefore, the energy of interaction between two solute atoms. But, because the dilatations produced are uniform, the energies of interaction are independent of distance: a solute atom interacts with *all* the others in the alloy. This is why the total energy of interaction $\sigma_i(c)$ of eqn. (65) is finite. This energy, being independent of the position of the atom, does not correspond to any *long range* force.

Interactions when solute atoms are in *contact* are probably small at small concentrations. At large concentrations, they favour ordered arrangements which relieve the stresses, thus leading to an apparent repulsion between solute atoms.

2.4. Liquid Alloys

The strain energies are usually assumed to disappear by melting, because atoms are more loosely bound in the liquid phase. The local

ordering of solute elements (Au Ni: Averbach *et al. loc. cit.*) and the positive anomaly of the entropy (Zn Cd: Lumsden *loc. cit.*) seem indeed to disappear by melting.

Wagner (1954) recently deduced the change ΔF in free energy by melting for a number of alloys from a thermodynamical study of the concentrations of the solidus and the liquidus at various temperatures. The following table shows that the observed values of ΔF are indeed large only for large size factor. They are, however, definitely smaller than the values computed from eqn. (67). This seems to indicate that only a fraction of the elastic strains disappears by melting. That some elastic strains subsist in the liquid phase would explain why metals with the same structure which do not mix in the liquid phase (Ag and Ni, Cu and Pb for instance) have always very different atomic sizes.

| | $T^{\circ}\text{K}$ | c | $ \delta /\bar{r}_s$ | ΔF comp. | ΔF obs. |
|------|---------------------|------|----------------------|--------------------|--------------------|
| AuNi | 1123 | 0.40 | 0.14 | 0.11 | 0.028 |
| AuCu | 1157 | 0.40 | 0.12 | 0.06 | 0.018 |
| NiPd | 1510 | 0.45 | 0.11 ₅ | 0.04 ₅ | 0.026 |
| PdFe | 1576 | 0.45 | 0.09 ₅ | 0.03 | 0.025 |
| RbK | 306 | 0.35 | 0.07 ₅ | 0.001 ₅ | 0.001 |
| FeCr | 1778 | 0.25 | 0.01 ₅ | 0.000 ₅ | 0.003 |
| FeCo | 1748 | 0.35 | 0.01 ₅ | 0.000 ₅ | 0.004 ₅ |
| NiFe | 1709 | 0.25 | 0.01 ₅ | 0.000 ₅ | 0.005 |

REFERENCES

- ABELÈS, F., 1953, *Comptes Rendus*, **237**, 796.
 ADAMS, E. N., 1952, *Phys. Rev.*, **85**, 41 ; 1953 a, *Ibid.*, **89**, 633 ; 1953 b, *J. Chem. Phys.*, **21**, 2012.
 AVERBACH, B. L., FLINN, P. A., and COHEN, M., 1954, *Acta Met.*, **2**, 92.
 BACHER, R., and GOUDSMIT, S., 1932, *Atomic Energy States* (New York).
 BARRETT, C. S., 1953, *Structure of Metals* (New York).
 BEARDEN, J. A., and FRIEDMAN, H., 1940, *Phys. Rev.*, **58**, 387.
 BIRCHENALL, C. E., and CHENG, C. H., 1949, *J. Met.*, 428.
 BLOCH, F., 1929, *Z. Phys.*, **52**, 555.
 BLOEMBERGEN, N., and ROWLAND, T. J., 1953, *Acta Met.*, **1**, 731.
 BOHM, D., and PINES, D., 1953, *Phys. Rev.*, **92**, 609.
 BROOM, T., 1954, *Advances in Physics*, **3**, 26.
 CARPENTER, L. G., 1953, *J. Chem. Phys.*, **21**, 2244.
 CAUCHOIS, Y., 1952, *Comptes Rendus*, **235**, 613 ; 1953, *Phil. Mag.*, **44**, 173.
 CHANDRASEKHAR, S., 1944, *Astrophys. J.*, **100**, 176.
 COHEN, A., 1933, *Z. Phys.*, **83**, 291.
 COLES, B. R., 1953, *Phil. Mag.*, **44**, 915.
 COTTRELL, A. H., 1948, *Theoretical Structural Metallurgy* (London).
 CRUSSARD, C., 1950, *Métaux et Corros.*, **25**, 203.
 DEXTER, D. L., 1952, *Phys. Rev.*, **87**, 768.
 DIENES, G. J., 1952, *Phys. Rev.*, **86**, 228.
 DRUYVESTYIN, M. J., 1954, private communication.

- ENDO, H., 1925, *Sci. Rep. Tohoku Univ.*, **14**, 479.
- ESHELBY, J. D., 1953, *J. Appl. Phys.*, **25**, 1249.
- FISHER, R. M., DULIS, E. J., and CARROLL, K. G., 1953, *J. Met.*, **5**, 690.
- FLETCHER, G. C., 1952, *Proc. Phys. Soc. A*, **65**, 192.
- FLINN, P. A., AVERBACH, B. L., and COHEN, M., 1953, *Acta Met.*, **1**, 664.
- FOURNET, G., 1953 a, *J. Phys. Radium*, **14**, 226 ; 1953 b, *Comptes Rendus*, **237**, 75 ; 1953 c, *Acta Met.*, **1**, 383.
- FRIEDEL, J., 1952 a, *Phil. Mag.*, **43**, 153 ; 1952 b, *Ibid.*, **43**, 1115 ; 1952 c, *Proc. Phys. Soc. B*, **65**, 769 ; 1953, *J. Phys. Radium*, **14**, 561 ; 1954 a, *Ibid.*, **15**, 433 ; 1954 b, *Ibid.*, to be published ; 1954 c, *Ann. de Phys.*, **9**, 158 ; 1954 d, *Physica*, to be published.
- FUCHS, K., 1935, *Proc. Roy. Soc. A*, **151**, 585.
- FUMI, F. G., 1954, private communication.
- GALT, J. K., 1949, *Phil. Mag.*, **40**, 309.
- GOLDMAN, J. E., 1953, *Rev. Mod. Phys.*, **25**, 108.
- GOMBÀS, P., 1949, *Stat. Theor. des Atoms* (Vienna).
- GUINIER, A., 1952, *Acta Crystallogr.*, **5**, 121.
- HAWORTH, J. B., and HUME-ROTHERY, W., 1952, *Phil. Mag.*, **43**, 513.
- HEITLER, W., 1936, *Quantum Theory of Radiation* (Oxford).
- HERBENAR, A. W., SIEBERT, C. A., and DUFFENDACK, O. S., 1950, *J. Met.*, 323, cf. UNDERWOOD, E. E., and AVERBACH, B. L., 1952, *J. Met.*, 1220.
- HILLIARD, J. E., AVERBACH, B. L., and COHEN, M., 1954, *Acta Met.*, to be published.
- HIMMLER, W., 1950, *Z. Phys. Chem.*, **195**, 244.
- HOUDREMONT, E., 1935, *Einführung in die Sonderstahlkunde* (Berlin), p. 183.
- HOWARTH, D. J., and JONES, H., 1952, *Proc. Phys. Soc. A*, **65**, 355.
- HUANG, K., 1948, *Proc. Phys. Soc.*, **60**, 161.
- HUME-ROTHERY, W., 1931, *The Metallic State* (Oxford) ; 1954, *Advances in Physics*, **3**, 149.
- HUNTINGTON, H. B., 1942, *Phys. Rev.*, **61**, 325 ; 1953, *Ibid.*, **91**, 1092.
- HUNTINGTON, H. B., and SEITZ, F., 1942, *Phys. Rev.*, **61**, 315.
- JASWON, M. A., HENRY, W. G., and RAYNOR, G. V., 1951, *Proc. Phys. Soc. B*, **64**, 177.
- JOHNSTON, R. W., 1954, *Thesis*, to be published in *Phys. Rev.*
- JONES, H., 1934, *Proc. Roy. Soc. A*, **144**, 255 ; 1953, *Phil. Mag.*, **44**, 907.
- JONES, H., and ZENER, C., 1934, *Proc. Roy. Soc. A*, **144**, 101.
- JONGENBURGER, P., 1953, *Phys. Rev.*, **90**, 710 ; 1954, *Appl. Sci. Res. B*, **3**, 237.
- KAYA, S., and KUSSMANN, A., 1931, *Z. Phys.*, **72**, 293.
- KEESOM, W. H., and KURRELMAYER, B., 1940, *Physica*, **7**, 1003.
- KLEPPA, O. J., 1954, private communication.
- KNIGHT, W. D., 1954, private communication.
- KOEHLER, J. S., 1954, private communication.
- KÖSTER, W., 1938, *Z. Metallk.*, **9**, 322 ; 1948, *Ibid.*, **39**, 145.
- KRÖNER, E., 1954, *Acta Met.*, **2**, 302.
- KUBASCHIEWSKI, O., and EVANS, E. LL., 1951, *Metallurgical Thermochemistry* (London).
- LANDOLT, H. H., and BÖRNSTEIN, R., 1931, *Tabellen* (Berlin).
- LAUE, M. V., 1914, *Ann. der Phys.*, **44**, 1197.
- LAWSON, A. W., 1947, *J. Chem. Phys.*, **15**, 831 ; 1950, *Trans. Amer. Soc. Metals*, **A**, **42**, 85.
- LEIGH, R. S., 1951, *Phil. Mag.*, **42**, 876.
- LINDE, J. O., 1939, *Dissertation* (Stockholm).
- LOWERY, H., WILKINSON, H., and SMARE, D. L., 1937, *Proc. Phys. Soc.*, **49**, 345.
- LUMSDEN, J., 1952, *Thermodynamics of Alloys* (London).
- MCDONALD, D. K. C., 1953, *J. Chem. Phys.*, **21**, 177.
- MASUMUTO, H., SAITO, H., and SUGIHARA, M., 1952, *J. Japan Inst. Met.*, **16** (7), 359 ; 1953, *Sci. Rep. Res. Inst. Tohoku Univ. A*, **5**, 213.

- MEIER, W., 1910, *Ann. der Phys.*, **31**, 1017.
 MEYERING, J. L., 1952, *Rev. Métall.*, **49**, 906.
 MORSE, P. M., 1932, *Rev. Mod. Phys.*, **4**, 577.
 MOTT, N. F., 1935, *Proc. Roy. Soc.*, **47**, 571 ; 1936, *Proc. Camb. Phil. Soc.*, **32**, 281 ; 1937, *Proc. Phys. Soc.*, **49**, 258 ; 1952, *Progr. Metal Phys.*, **3**, 76 ; 1953, *Phil. Mag.*, **44**, 187.
 MOTT, N. F., and GURNEY, R. W., 1948, *Ionic Solids* (Oxford).
 MOTT, N. F., and JONES, H., 1936, *Metals and Alloys* (Oxford).
 MOTT, N. F., and MASSEY, H. S. W., 1949, *Atomic Collisions* (Oxford).
 NABARRO, F. N. R., 1940, *Proc. Roy. Soc. A*, **175**, 519.
 NIESSEN, K. F., 1939, *Physica*, **6**, 1011.
 OELSEN, W., and MIDDEL, W., 1937, *Mitt. K.-Wilh.-Inst. Eisenforsch.*, **19**, 1.
 ORIANI, R. A., 1953, *Acta Met.*, **1**, 448.
 PECKAR, S., 1946, *J. Phys. USSR.*, **10**, 431.
 PETERLS, R., 1933, *Z. Phys.*, **80**, 763.
 PINÈS, B. I., 1941, *Jurnal eksp. teor. fiziki*, **11**, 147.
 POCHAPSKY, T. E., 1953, *Acta Met.*, **1**, 747.
 PRATT, J. N., and RAYNOR, G. V., 1951, *Proc. Roy. Soc. A*, **205**, 103.
 RICHARDSON, F. D., and DENNIS, W. E., 1953, *Trans. Faraday Soc.*, **49**, 171.
 ROBINSON, K., 1953, *Acta Crystallogr.*, **6**, 854.
 ROBINSON, K., and BLACK, P. J., 1953, *Phil. Mag.*, **44**, 1392.
 RUDMAN, P. S., FLINN, P. A., and AVERBACH, B. L., 1953, *J. Appl. Phys.*, **24**, 365.
 SCHWAB, G. M., 1946, *Trans. Faraday Soc.*, **42**, 689.
 SEITZ, F., 1940, *Theory of Solids* (New York) ; 1946, *Rev. Mod. Phys.*, **18**, 384.
 SHINODA, G., SUZUKI, T., and KATO, S., 1954, private communication.
 SHINOHARA, S., 1952, private communication ; 1954, *Progress in Theoretical Physics*, to be published.
 SHULL, C. G., 1953, private communication ; 1954, *Congrès Solvay*.
 SKINNER, H. W. B., 1932, *Proc. Roy. Soc. A*, **135**, 84 ; 1933, *Ibid.*, **140**, 277.
 SKINNER, H. W. B., and JOHNSTON, J. E., 1937, *Proc. Roy. Soc. A*, **161**, 420.
 SLATER, J. C., 1936, *Phys. Rev.*, **49**, 537 ; 1949, *Ibid.*, **76**, 1592 ; 1951, *Ibid.*, **81**, 385 ; 1953, *MIT Sol. state techn. rep.* No. 4, 5.
 SLATER, J. C., and KOSTER, G. F., 1954, *MIT Sol. state quart. progr. rep.*, 15th Jan., 4.
 SMITHELLS, C. J., 1949, *Metals Reference Book* (London).
 SOMMERFELD, A., 1928, *Z. Phys.*, **47**, 1.
 STOBEE, M., 1930, *Ann. der Phys.*, **7**, 661.
 TAYLOR, W. H., 1952, *Abingdon Conference Report*.
 TIBBS, S. R., 1939, *Trans. Faraday Soc.*, **35**, 1471.
 TIMOSCHENKO, S., 1934, *Theory of Elasticity* (New York), p. 324.
 TOWNSEND, J. R., 1953, *Phys. Rev.*, **92**, 556.
 VAN DER WAERDEN, B. L., 1932, *Quantenmechanik* (Berlin), p. 5.
 VARLEY, J. O., 1953, *Thesis*, to be published in *Phil. Mag.*
 VOGT, E., 1951, *Z. Metallk.*, **42**, 155 ; 1954, *Appl. Sci. Res. B*, **4**.
 VOGT, E., and HARMS, B., 1943, *Ann. der Phys.*, **42**, 501.
 VOLTERRA, V., 1930, *Theory of Functionals* (London).
 VON LAUE, M., 1914, *Ann. der Phys.*, **44**, 1197.
 WAGNER, C., 1952, *Thermodynamics of Alloys* (New York) ; 1954, *Acta Met.*, **2**, 242.
 WALKER, C. B., BLIN, J., and GUINIER, A., 1952, *Comptes Rendus*, **235**, 254.
 WANNIER, G. H., 1937, *Phys. Rev.*, **52**, 191.
 WATSON, C. N., 1922, *Bessel Functions* (Cambridge), p. 368.
 WEISS, P., and KLEMM, W., 1940, *Z. anorg. Chemie*, **245**, 288.
 WEYLL, H., 1912, *Math. Ann.*, **71**, 41.
 WILSON, A. H., 1953, *Theory of Metals* (Cambridge).
 YVON, J., 1945, *Cah. Phys.*, **28**, 1.

Annals of Science

A QUARTERLY REVIEW OF
THE HISTORY OF SCIENCE
SINCE THE RENAISSANCE

EDITORS

D. McKIE, D.Sc., Ph.D.,
University College, London.

HARCOURT BROWN,
M.A., Ph.D.,
Brown University, Providence, R.I.,
U.S.A.

H. W. ROBINSON,
Former Librarian,
Royal Society of London.

N. H. de V. HEATHCOTE,
B.Sc., Ph.D.,
University College, London.

ANNUAL SUBSCRIPTION

£3 3s. 0d.

OR

18s. 0d.

PER PART

POST FREE



THE MATHEMATICAL WORKS OF JOHN WALLIS, D.D., F.R.S.

by

J. F. SCOTT, Ph.D., B.A.

"His work will be indispensable to those interested in the early history of The Royal Society. I commend to all students of the Seventeenth Century, whether scientific or humane, this learned and lucid book."—Extract from foreword by Prof. E. N. da C. Andrade, D.Sc., Ph.D., F.R.S.

Recommended for publication by University of London

12/6 net

Printed and Published by

TAYLOR & FRANCIS, LTD.
RED LION COURT, FLEET STREET, LONDON, E.C.4.

RECEIVED
JAN 10 1954
U.S. DEPARTMENT OF
THE ARMY
WASHINGTON, D.C.

RECEIVED JAN 10 1954

10 10 54

RECEIVED JAN 10 1954
U.S. DEPARTMENT OF
THE ARMY
WASHINGTON, D.C.